

# **CHEMICAL ANALYSIS OF ROCKS AND MINERALS**

**NEW ANALYTICAL METHODS DEVELOPED FOR SOME MAJOR  
AND MINOR COMPONENTS**

Risto Saikkonen



**Geological Survey of Finland**

**Espoo 1996**

**CHEMICAL ANALYSIS OF ROCKS AND MINERALS  
NEW ANALYTICAL METHODS DEVELOPED FOR SOME MAJOR  
AND MINOR COMPONENTS**

by

Risto Saikkonen

**Academic Dissertation**

To be presented with the permission of the Faculty of Science of the University of Helsinki  
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Geological Survey of Finland

Chemical Laboratory

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**Saikkonen, Risto 1996.** Chemical analysis of rocks and minerals - new analytical methods developed for some major and minor components. Espoo: Geological Survey of Finland. 47 pages, 2 figures, 5 tables and one appendix.

The study examines a number of geological samples the chemical analysis of which requires in-depth knowledge of preparation, decomposition and determination techniques. Rock, mineral and meteorite samples were analysed with modified classical wet-chemical methods and more modern instrumental methods (Publications I-V). The Summary presents the first published total analysis of the Malampaka meteorite (an olivine-bronzite chondrite). Chemical analyses of some mineral samples are also presented for the first time.

In the course of the work, analytical methods were developed and studied for rocks, minerals and other geological materials such as meteorites. To establish the accuracy, precision and detection limits of these methods, they were compared with existing methods using domestic and international reference samples.

The development and investigation of analytical methods for water, ferrous iron and carbon are presented in separate publications (VI-VIII). The determinations of these components are discussed in the Summary in those respects not dealt with above. Determinations of halogens, sulphur and loss on ignition are discussed on the basis of the literature and practical experience.

**Key words** (Georef Thesaurus, AGI): chemical analysis, wet methods, atomic absorption, emission spectroscopy, infrared spectroscopy, rocks, minerals, meteorites, chemical elements, water, ferrous iron, carbon, halogens, sulfur, loss on ignition.

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**FOREWORD**

This work comprises the following papers published previously:

**I**            **Laajoki, K. and Saikkonen, R., 1977.** On the geology and geochemistry of the Precambrian iron formations in Väyrylänkylä, south Puolanka area, Finland. Part Geochemistry. Geological Survey of Finland, Bulletin 292, 78-123.

**II**            **Danielsson, R. and Saikkonen, R., 1985.** Chemical analysis of USGS-W-2, USGS-DNC-1 and USGS-BIR-1 standard rocks. Geological Survey of Finland, Report of Investigation 70. 13 p.

**III**            **Lahti, S. and Saikkonen, R., 1985.** Bityite 2M1 from Eräjärvi compared with related Li-Be brittle micas. Bulletin of the Geological Society of Finland 57, Part 1-2, 207-215.

**IV**            **Lahti, S. and Saikkonen, R., 1986.** Kunzite from the Haapaluoma pegmatite quarry, western Finland. Bulletin of the Geological Society of Finland 58, Part 2, 47-52.

**V**             **Kinnunen, K. A. and Saikkonen, R., 1983.** Kivesvaara C2 chondrite: silicate petrography and chemical composition. Bulletin of the Geological Society of Finland 55, Part 1, 35-49.

**VI**            **Saikkonen, Risto J., 1990.** Determination of water in silicate rock samples by combustion and infrared absorption. Bulletin of the Geological Society of Finland 62, Part 1, 71-77.

**VII**            **Saikkonen, Risto J. and Rautiainen, Irja A., 1993.** Determination of ferrous iron in rock and mineral samples by three volumetric methods. Bulletin of the Geological Society of Finland 65, Part 1, 59-63.

**VIII Saikkonen, Risto J. and Rautiainen, Irja A., 1990.** Determination of total carbon and non-carbonate carbon in rock samples by an infrared absorption method. Bulletin of the Geological Society of Finland 62, Part 2, 149-156.

These publications are referred to in the Summary with Roman numerals I-VIII.

Publication I deals with the geochemistry of the Precambrian sedimentary iron formations at Väyrylänkylä, Puolanka, with the aid of total rock, partial rock and mineral analyses.

Publication II presents new, previously unpublished analytical data on three reference rock samples of the USGS, i.e., W-2 diabase, DNC-1 diabase and BIR-1 basalt. The analytical data obtained are compared with those reported by geolaboratories abroad.

Publication III examines in detail the bityite mineral,  $\text{Ca}_{1.93} \text{K}_{0.03} \text{Na}_{0.02} (\text{Li}_{1.19} \text{Al}_{3.68} \text{Mg}_{0.35} \text{Fe}_{0.13}) (\text{Al}_{1.53} \text{Be}_{2.21} \text{Si}_{4.26}) \text{O}_{19.30} (\text{OH})_{4.54} \text{Fe}_{0.16}$ , which occurs in a pegmatite vein at Eräjärvi. The mineral had not previously been described from Finland.

Publication IV describes a purple, transparent spodumene from Peräseinäjoki, Finland, which turned out to be a gem-quality kunzite.

Publication V is a study on the Kivesvaara meteorite found in Paltamo, northern Finland, in 1968. In chemical and mineralogical composition and in structure the meteorite is a rare C2-class carbon-bearing chondrite.

Publication VI describes a new method for determining water in rock and mineral samples based on infra-red absorption.

Publication VII examines three methods for determining ferrous iron and discusses their accuracy and precision, and possible sources of error.

Publication VIII reports the determination of total carbon with infra-red absorption spectrometry and that of non-carbonate carbon in a chemically pretreated sample using the same method.

## 1 INTRODUCTION

The chemical analysis of rocks and minerals determines the concentrations of elements and certain components. Geological investigations, which are often an integral part of exploration for resources of raw materials in bedrock, require increasingly detailed information on the chemical composition of rocks and minerals. Although often covered, bedrock occurs everywhere on the globe. It is composed of different lithologies (rocks), which in turn are composed of minerals. Most minerals, of which over 2000 species are known, are crystalline compounds. The majority are rare and thus unimportant as rock-forming constituents. The major minerals of rock types number only a few tens and these are mainly silicates.

The established practice in classical rock analysis is to determine the composition of 13-18 elements. This type of analysis is called total analysis. Chemical analyses of rocks are usually expressed as weight percents of oxides for the major elements. It is assumed, in the absence of oxygen determinations, that the major cations are accompanied by a stoichiometrically equivalent amount of oxygen. Most rocks are silicate rocks composed of silicate minerals; total analysis is then called silicate analysis and includes the following major and minor components: silica, titanium dioxide, aluminium oxide, manganese oxide, iron(III) oxide, iron(II) oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide, phosphorus pentoxide, carbon dioxide, constitutional water and moisture water. These components are analysed because they are the ones used in petrochemical calculations of the rocks and because it is easier to compare rock analyses with each other if the same components are determined and if they are reported in the same order (Lightfoot 1983, Mueller & Saxena 1977). Sulphur, fluorine and chlorine concentrations and loss on ignition are also often determined. The concentrations of major components usually exceed 1%, and those of minor components are in the range 1-0.01%. The concentrations of trace components are less than 0.01% and are frequently reported in parts per million, ppm, or ng/g. All the components included in the total analysis of rocks or minerals may be called major components. Today, an ever increasing number of trace elements can be determined (Table 1). For silicate minerals, the concentrations of components are reported in the same way as they are for silicate rocks. The components of non-silicate minerals and rocks may differ and these are often reported in order of importance.



Mineral analyses are used to calculate the formula for the mineral being investigated, to check the "purity" of the mineral, e.g. to establish the extent to which two minerals are mixed with each other in solid solution, and to gauge large compositional variations in minerals. The above also applies to special geological samples such as meteorites. The elements determined at any one time depend on the purpose for which their concentrations are used or needed (see Johnson & Maxwell 1981, Potts 1987).

Table 1 gives the total composition and several trace element concentrations of a silicate rock, granite G-I, which was the first international reference rock sample (Fairbairn 1951). The components of the total analysis are summed. The sum is one of the criteria of the success of total analysis. It does not, however, guarantee that the data on the single components are correct. Opinions differ about the magnitude of the sum of a good analysis but  $100\% \pm 0.5\%$  is universally considered acceptable. The analysis sum should be corrected by subtracting the amount of oxygen corresponding to sulphide sulphur and fluorine and chlorine, because the elements that occur as sulphides, fluorides or chlorides are reported as oxides. The sulphide correction can be done only if the mineral composition of the sample is known (Jeffery & Hutchison 1983).

The analytical method used here includes chemical pretreatment of the sample and the method of determination plus the output of data. Sample preparation with its various stages takes place between the analytical procedure and sampling. The method of determination includes the pretreatment technique of a portion of the sample, the instrumental or other determination and the output of data. The quality of the analytical methods depends on the quality of all the contributing factors. The quality of the methods can be assessed with various parameters deduced from the analytical data obtained (see Johnson 1993, Potts 1993). Thanks to the rapid progress made in instrumentation, automatics and data processing, well-equipped laboratories can now produce more and more rock analyses with an increasing number of trace elements. Assuring the quality of analytical data has thus become increasingly important, and laboratories are required to report on and interpret the quality and applicability of their analytical data. Correct use and interpretation of analytical data help guarantee the success of geological investigations and interpretations.

**Table 1.** Compositions of USGS granite sample, G-1, which was the first international geological reference sample in the world (Fairbairn et al. 1951). Numerical values for the concentrations of major, minor and trace constituents are from the paper of Govindaraju (1989).

Major and minor constituents %		Trace elements ng/g			
SiO <sub>2</sub>	72.51	Ag	0.044	Mo	6.8
TiO <sub>2</sub>	0.26	As	0.7	N	59
Al <sub>2</sub> O <sub>3</sub>	14.23	Au	0.0032	Nb	22.6
Fe <sub>2</sub> O <sub>3</sub>	0.86	B	1.6	Nd	57
FeO	0.97	Ba	1080	Ni	3.4
MnO	0.03	Be	3	Os	0.00011
MgO	0.36	Bi	0.05	Pb	46
CaO	1.37	Br	0.14	Pd	0.0019
Na <sub>2</sub> O	3.33	C	200	Pr	17
K <sub>2</sub> O	5.51	Cd	0.059	Pt	0.08
P <sub>2</sub> O <sub>5</sub>	0.08	Ce	173	Rb	214
H <sub>2</sub> O <sup>+</sup>	0.34	Cl	40	Re	0.00063
H <sub>2</sub> O <sup>-</sup>	0.05	Co	2.3	S	130
CO <sub>2</sub>	0.07	Cr	20	Sb	0.3
F	0.07	Cs	1.6	Sc	2.8
S	0.01	Cu	12	Se	0.007
Others	0.29	Dy	2.4	Sm	8.3
Sum	<u>100.34</u>	Er	1.3	Sn	3.2
-O/F, S, Cl	0.03	Eu	1.22	Sr	248
Sum <sub>(corr.)</sub>	<u>100.31</u>	F	680	Ta	1.5
Fe <sub>2</sub> O <sub>3</sub> total	1.95	Ga	19,5	Tb	0.58
		Gd	4.8	Th	51
		Ge	1.12	Tl	1.23
		Hf	5.4	Tm	0.15
		Hg	0.085	U	3.4
		Ho	0.39	V	18
		I	0.035	Yb	1
		In	0.0252	Zn	45
		Ir	0.002	Zr	201
		La	105		
		Li	21.3		
		Lu	0.156		

From the early years of this century, the chemical analysis of rocks and minerals has been made with classical wet-analytical methods. In classical analysis, elements are precipitated from the solution as successive group precipitates and then determined mainly with gravimetric methods. In the 1950s, rapid methods based largely on optical spectroscopy, complexometric titration and flame emission were developed alongside those of classical analysis. Modified classical methods and some rapid methods are still

used for the total analyses of reference rock and mineral samples required by instruments and other non-routine samples and for determining the concentrations of some elements and components. Since the 1960s, X-ray fluorescence spectrometry (wavelength dispersive and energy dispersive), instrumental neutron activation analysis and flame atomic absorption and emission spectrometry and graphite furnace AA spectrometry, since the 1970s, plasma atomic emission spectrometry and since the 1980s, plasma mass spectrometry, have replaced many of the classical and rapid methods. Today, chemical analyses of rocks and minerals are made on instruments capable of determining up to 30-40 elements simultaneously or in rapid succession. Among the techniques now in common use are the X-ray fluorescence analysis (XRF, in this study WD-XRF), flame atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).

However, not all the components of total rock and mineral analyses can be determined with these instruments. The determinations of elements or components that cannot be made with the above instruments, or which for some other reason are made separately, are here called individual determinations. Water, ferrous iron and carbon are the most common components analysed in this way. For rocks and minerals, halogen and sulphur concentrations and loss on ignition are also often measured as individual determinations.

The water in rocks and minerals occurs as moisture and constitutional or essential water. There are several methods for determining water, the most common of which are those based on gravimetry, titrimetry and infra-red (IR) spectrometry (Section 3.1, VI).

In rock and mineral samples, iron mostly occurs in oxidation states +II and +III. After the concentration of ferrous iron has been determined, the concentration of ferric iron can be calculated as a difference:  $\text{Fe}(\text{total}) - \text{Fe}(\text{ferrous}) = \text{Fe}(\text{ferric})$ . Iron(II) is usually determined by titrimetry or spectrophotometry. There are very few methods for determining iron(III) (Section 3.2, VII).

Carbon occurs in rocks and minerals as carbonate carbon and non-carbonate carbon, both of which are measured as individual determinations. The methods used for

determining the total carbon concentration are based on combustion of the sample, in the course of which the elemental carbon converts into carbon dioxide and the total carbon can be measured as carbon dioxide. The carbon concentration in carbonate is obtained by liberating and measuring the carbon dioxide from carbonates. Non-carbonate carbon can be obtained from the difference between total and carbonate carbons but can also be determined individually. Non-carbonate carbon is composed of graphite and organic carbon (Section 3.3, VIII).

Halogens can be analysed by XRF although individual determinations are also frequently made with an ion-selective electrode, ion-chromatography and spectrophotometry. Neutron activation is also used (Section 3.4). The total sulphur in a sample can also be analysed by XRF, but it is most commonly measured as an individual determination by combusting sulphur into oxide and measuring the amount of sulphur dioxide thus formed. The sulphide and sulphate sulphurs in a sample can be analysed individually with wet-chemical methods, too (Section 3.4). Loss on ignition (LOI) is determined gravimetrically by igniting the sample at a high temperature (1000-1200°C) and measuring the loss in weight. LOI indicates the amount of volatile components in the sample. These components include e.g. water (both moisture,  $H_2O$ , and essential water,  $H_2O^+$ ), carbon dioxide ( $CO_2$ ), sulphur (S) and organic matter (Section 3.4).

## **2                   CHEMICAL ANALYSES OF ROCK, MINERAL AND CERTAIN SPECIAL SAMPLES**

This section deals with the preparation and chemical analysis of rock and mineral samples and certain special samples such as meteorites. An analytical package containing modified classical methods and new methods is described, and a brief look is taken at AAS, XRF and ICP-AES.

## 2.1 Sample preparation

Variations in the analytical results of rock, mineral and special samples such as meteorites, are controlled by variations in the geology, mode of taking and transporting the sample, preparation of the sample and analytical factors. Laboratories see to the preparation and analysis of samples. Sample preparation is the procedure between sampling and chemical analysis. Sampling has attracted considerable attention recently, partly due to the intensification of exploration for gold. The "nugget" (or single particle) phenomenon is a reminder of the importance of correct sample selection and preparation. The result of a chemical analysis and the geological inferences drawn from it are no better than the sample from which the data derive. The total error or analytical variation in results is the sum of all sub-errors. (Richardson 1993).

In preparation, a field rock sample, the size of which depends on the grain size and homogeneity of the material, is reduced to a size, shape and weight appropriate for analysis. The field sample is usually cut in two with a rock cutter (or "guillotine"), then crushed in a jaw crusher and/or roll mill and pulverized in a disc mill. At intervals, the size of the sample is reduced by splitting it into portions of equal size and taking only one of these for further treatment. The sample should, however, retain its homogeneity throughout the milling. The sample thus obtained, with a weight of 30-200 g and a grain size of 100-200 mesh (0.147-0.074 mm), should represent the parent sample as closely as possible. Contamination due to machinery, the environment or other samples is difficult to eliminate completely and should be kept as low as possible. In trace element determinations in particular, error due to contamination may dominate the preparation error. Other preparation errors include loss of sample and volatile components and the oxidation of ferrous iron in crushing, milling and homogenization. The finer a sample is ground the longer it is in contact with air, the more moisture it gets from air and the larger the part of ferrous iron that is oxidized into ferric iron. Heating a sample during milling also enhances the oxidation of ferric iron and may result in loss of water of crystallization. Small samples such as minerals and meteorites are usually crushed in steel or diamond mortars and ground manually in an agate mortar (Saheurs et al. 1993).

The separation of mineral grains from a rock sample begins with the crushing and grinding of the sample to a particle size smaller than that of the smallest grain of the mineral to be studied. The most common grain size is 100-200 mesh. The separation of minerals is based on the difference between their magnetic properties and specific gravities. Picking minerals under a microscope is a very useful technique. Tiny mineral grains, e.g. zircon grains in micas or chlorite grains in feldspars, may occur as inclusions in the mineral being studied. In such cases it is impossible to obtain pure mineral matter, and the mineral analysis has an error component (Hutchison 1974, Papers III and IV).

Meteorites are divided into three main groups: stony, iron-stony and iron meteorites. Preparation of meteorite samples depends to a great extent on the concentration of native iron in the meteorite, and thus it is often very difficult to obtain a representative sample. Stony meteorites without native iron are crushed and milled like silicate rocks (III). The fusion crust formed when a meteorite falls must first be removed. Stony meteorites with metallic iron, and stony iron meteorites are often divided magnetically and/or by picking under a microscope into metallic and stony portions that can be analysed separately. Samples are taken from iron meteorites by drilling or crushing, and their purity is checked under the microscope. Metallic portions and inclusions are sometimes analysed separately. The total analysis is obtained by combining the subanalyses once the proportion of inclusions in the meteorite has been calculated from their surface areas (Easton 1972). The metallic portions of meteorites can be milled together with the stony portions by grinding the sample at the temperature of liquid air (Berry & Rudowski 1965). The metallic portions can be evaporated as chlorides with a dry chlorine gas, in which case stony matter is obtained as a residue (Moss et al. 1961).

## 2.2 Rock analysis

For decades, the chemical analysis of rocks and minerals has been made with classical wet methods in which the powdered sample is dissolved with the aid of fusion or acids. In the classical analysis, elements are precipitated from the solute as successive groups and their concentrations determined, commonly with gravimetric methods. Over the years there have been many changes and refinements to the classical silicate analysis (Dittler 1933, Hillebrand & al. 1953, Maxwell 1968, Jeffery & Hutchison 1983). In the 1950s, rapid methods seeking to determine as many components as possible from the same solute without separations and precipitations were developed parallel to the classical analysis. These methods were largely based on optical spectroscopy, complexometric titration and flame emission (Shapiro & Brannock 1956). Both classical and rapid methods are still used for certain elements. Modified classical methods are also used for the accurate total analyses of reference rock and mineral samples required by analytical instruments. The first international reference rock samples were G-1, granite and W-1, diabase (Fairbairn 1951). Today there are over three hundred international geological reference samples (rocks, minerals, soils, ores etc.) (Govindaraju 1994). The Geological Survey of Finland (GSF) has participated in the elaboration of many reference samples, with the author as a member of the team of chemists involved.

Figure 1 presents the modified classical methods employed in the chemical laboratory of GSF and a scheme for the main component analysis of silicate rocks and minerals. This scheme, which includes newer methods, has also been applied to other geological samples, e.g. meteorites (I-V). Main component analysis consists of a main portion and individual determinations. The procedure of the main portion is briefly as follows. Powdered sample is dried at 110°C, and weighed to obtain the moisture (H<sub>2</sub>O) content. The sample is then fused with sodium carbonate in a platinum crucible at 1100°C. The fusion cake is dissolved in dilute hydrochloric acid, and silicon is determined gravimetrically by separating it from the solute as silica hydrogel, which is then ignited into silica for weighing. Mixed oxides, ammonia group or "R<sub>2</sub>O<sub>3</sub>" are precipitated from the filtrate with ammonia. The ignited and weighed oxide precipitate (Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, etc.) is dissolved with pyrosulphate flux and the solution is

made acidic with sulphuric acid. The residual silicon is determined from this solution gravimetrically, and the total iron and titanium colorimetrically - iron as the yellow ferric chloride complex and titanium with the Tiron reagent. The aluminium concentration is obtained by subtracting from the total of the mixed oxides the combined total of other elements present. Calcium is precipitated from the filtrate of the hydroxide precipitate as oxalate, and magnesium is then precipitated as ammonium-magnesium phosphate. Calcium is weighed as calcium carbonate or oxide, and magnesium as magnesium pyrophosphate.

The second subsample is dissolved in hydrofluoric, nitric and perchloric acids. Concentrations of sodium and potassium are determined from the solute thus obtained by flame emission spectrophotometry (FAES) (Asklund et al. 1966) or flame AAS (Van Loon 1980). Those of manganese and phosphorus are determined colorimetrically as permanganate (Langmyhr & Graff 1965) and molybdovanado phosphoric acid complex (Shapiro & Brannock 1956).

The sample is analysed for water (Section 3.1, VI), ferrous iron (Section 3.2, VII), carbon dioxide (Section 3.3, VIII), native carbon (Section 3.3, VIII), sulphur, fluorine and chlorine as independent determinations. The water content of the sample is measured by the IR method (VI). The constitutional water is obtained by subtracting the moisture water from the total water (VI). The concentration of ferric iron is calculated by subtracting the concentration of ferrous iron from that of total iron (VII). This scheme for the complete chemical analysis of silicate rocks is an outcome of continuous development. Several geoanalysts have published their rock analytical methods and schemes (see e.g. Washington 1932, Hillebrand et al. 1953, Peck 1964, Maxwell 1968, Kirschenbaum 1983).

Most routine chemical analyses of rocks and minerals are currently made with instruments permitting the simultaneous or rapid successive determination of several elements. Instruments in common use include the X-ray fluorescence spectrometer, the atomic absorption spectrometer and the inductively coupled plasma spectrometer.





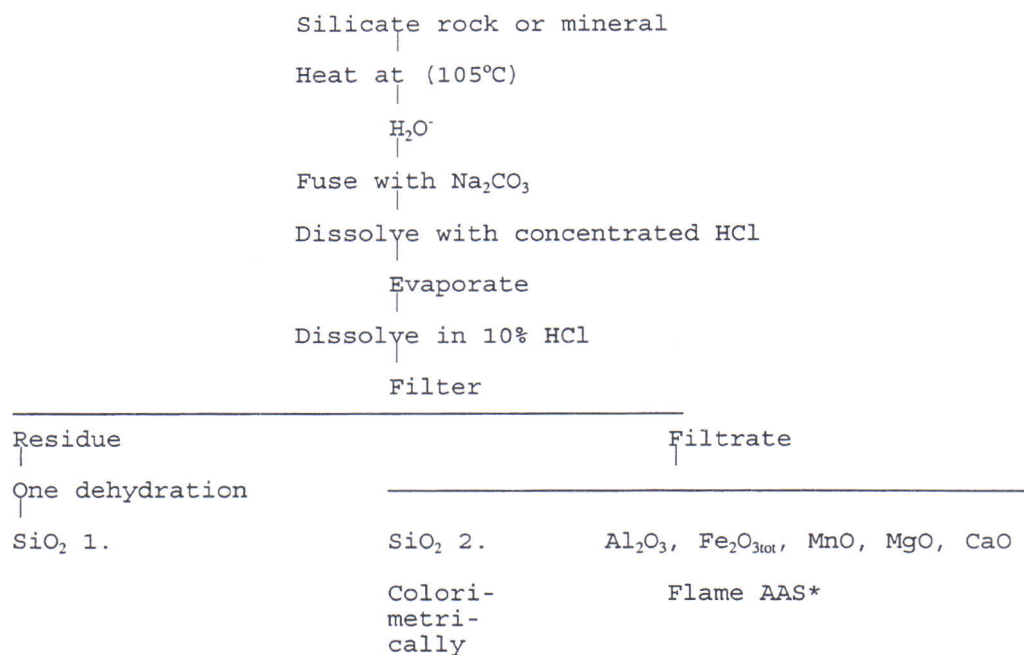
Samples can be analysed for several major, minor and trace elements by XRF. Powdered sample is converted into a glass disk by fusion or is compressed with a binder into a briquette. Geological samples can be analysed by XRF for Si, Ti, Al, Fe<sub>tot</sub>, Mn, Mg, Ca, Na, K, P, S, F, Cl and many other elements (Table 2) (Potts 1993, Longerich 1995).

For flame AAS and ICP-AES analyses, the sample is brought into solution. The resulting solution is usually made with lithium metaborate fusion or acids. Samples are analysed successively for Si, Al, Mn, Mg, Ca, Na and K by AAS from the same sample solution (Table 2) (Angino & Billings 1972, Slavin 1982).

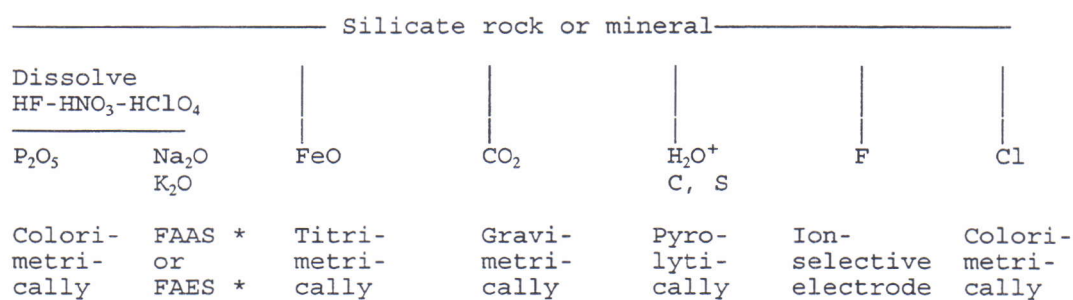
In the 1970s and '80s the present author and his colleagues in GSF developed an analytical scheme for rock and mineral samples based on flame AAS (Fig. 2). In this scheme the bulk of silicon is removed from the solution with a single precipitation, and the filtrate (0.5 g/250 ml made acidic with HCl) is analysed colorimetrically for residual silicon and by flame AAS for aluminium and manganese. Total iron, calcium and magnesium often require dilution. In the same years the flame AAS or flame AES methods for several elements, e.g. Li, Rb, Cs, Be, Sr, Cr, Co, Ni, Cu, Zn and Cd, in a filtrate and in HF-HNO<sub>3</sub>-HClO<sub>4</sub> solution were developed by the present author and his colleagues. The standard solutions are made taking into account the interference caused by the matrix and ionization (Saikkonen 1967, 1968, 1969, 1970a, 1970b and Papers II, III, IV and V).

In ICP-AES analyses lithium metaborate is commonly used as flux. The fusion cake is dissolved in dilute nitric or hydrochloric acid. Perhaps the most widely used method of dissolution is the acid digestion using mixtures of HF-HClO<sub>4</sub> and/or HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> acids in an open vessel from which silicon evaporates as SiF<sub>4</sub>. Decomposition is more effective when done in a closed vessel at pressure. Silicon then remains in solution and so can be determined. The solute is directed into a hot plasma and, with the aid of standard solutions, the concentrations of up to 40 elements are determined simultaneously from the emitting radiation with a spectrometer. For total analyses, samples can be analysed for Si, Ti, Al, Fe<sub>tot</sub>, Mn, Mg, Ca, Na, K and P by ICP-AES (Table 2) (Thompson & Walsh 1989, Jarvis & Jarvis 1992).

**Figure 2.** A scheme for main component analysis of silicate rocks and minerals developed at the Geological Survey of Finland in the 1970s and '80s. "Main" portion analysis with flame AAS from the solution after one precipitation of silicon. Components requiring individual determination.



COMPONENTS REQUIRING INDIVIDUAL DETERMINATION:



\* with flame AAS or flame AES, also trace elements: Li, Rb, Cs, Be, Sr, Cr, Co, Ni, Cu, Zn, Cd, etc.

**Table 2.** Element oxide concentrations (%) of the international rock reference sample W-2 (diabase); according to the literature, with modified classical and some other methods, XRF, flame AAS and ICP-AES. Standard deviations calculated from six successive determinations.

	LIT. <sup>a</sup>	CLASS <sup>b</sup>	XRF <sup>c</sup>	AAS <sup>d</sup>	ICP-AES <sup>e</sup>
SiO <sub>2</sub>	52.44	52.60±0.10	52.95±0.17	52.47±0.45	52.22±0.21
TiO <sub>2</sub>	1.06	1.04±0.01	1.06±0.01	1.06±0.01	1.05±0.01
Al <sub>2</sub> O <sub>3</sub>	15.35	15.51±0.13	15.39±0.19	14.83±0.14	15.40±0.13
Fe <sub>2</sub> O <sub>3tot</sub>	10.74	10.75±0.03	10.85±0.09	10.60±0.01	10.98±0.32
Fe <sub>2</sub> O <sub>3</sub>	1.52	1.41±0.04			
FeO	8.31	8.39±0.02			
MnO	0.16	0.16±0.00	0.16±0.00	0.16±0.00	0.15±0.00
MgO	6.37	6.63±0.06	6.28±0.07	6.24±0.05	6.03±0.04
CaO	10.87	10.74±0.02	11.33±0.02	10.98±0.02	10.80±0.01
Na <sub>2</sub> O	2.14	2.11±0.01	2.11±0.03	2.18±0.01	2.24±0.05
K <sub>2</sub> O	0.62	0.63±0.01	0.65±0.01	0.60±0.01	0.61±0.02
P <sub>2</sub> O <sub>5</sub>	0.13	0.11±0.00	0.14±0.01		0.24±0.02
H <sub>2</sub> O <sup>+</sup>	0.55	0.58±0.02			
H <sub>2</sub> O <sup>-</sup>	0.23	0.15±0.00			
CO <sub>2</sub>	0.06				
S	79 ppm				
F	205 ppm				
Cl	190 ppm				

a. Potts et al. 1992 b. GSF, analysed by the present author (Paper II), c. laboratory USGSR/XRF (Flanagan 1984), d. laboratory BIO/AAS (Flanagan 1984), e. laboratory UIND/ICP-AES (Flanagan 1984).

The compositions of and some information on rock and mineral samples analysed in the chemical laboratory are stored in the database of GSF. The rock and mineral analysis data base, KALTIE, contains 3274 chemical analyses of Finnish rocks and minerals, which were obtained in 1905-1992 with classical and instrumental methods. The general information (number of sample and analysis, location, rock types, geologist, analyst, publication) and the analysis information (main and trace constituents, method of chemical analysis) on the rocks and minerals are stored in this relational database (Gustafsson & Saikkonen 1994).

The main-portion analysis and the analysis of the components requiring individual determination (Fig. 1) were tested and investigated in publication II. Agreement between the results of this study and the "best estimates" given by F.J. Flanagan was good (Flanagan 1984). The coefficient of variation of the data for ten constituents was 0.1-1% and for two constituents over 1%. (Table 2). The precision of the classical silicate analysis has also been assessed by Flanagan and Kirschenbaum (1984), who analysed reference rock samples for 15 elements or components using classical chemical methods. According to them, the variation of the determinations (CV = 0.2-1%) will be the same for sample portions analysed as a group or analysed over some time interval.

The precision of a technique depends upon many factors e.g. sample preparation, matrix and interference effects and their correction, and instrumental drift during an operation. The precision for an element is generally related to the concentration. Comparison of the precision of different techniques is therefore difficult. The precisions of XRF, flame AAS and ICP-AES presented here were taken from the literature and so are comparable only to some degree.

The precisions of XRF rock analyses are about the same as those of the classical silicate analysis (CV = 0.2-1%) for Si, Ti, Al, Fe<sub>tot</sub>, Mn, Mg, Ca, Na and K, when samples are made into glass disks after fusion with a specified lithium tetraborate/metaborate flux (Ramsey et al. 1995). It is well known that the lightest elements (particularly Na, Mg, Al, and Si) do not usually yield highly accurate and precise results when from pressed pellets because of mineralogical effects. The precisions for the heavy major elements, K, Ca, Ti, Mn, and Fe, are very similar to those obtained with a more accurate and precise sample preparation by fusion (Longerich 1995). According to the data obtained at the chemical laboratory of the GSF, the coefficients of variation of XRF determinations are < 1% for Si, Ti, Al, Fe, Mg, Ca and Na, and 1-3% for Mn, K and P (method code 175X: multi-element, over 40 elements, determination from powder pellets of sample) (Maija Hagel-Brunnström 1995, unpublished results).

For the AAS determinations, the coefficients of variation are about 0.1-3% for major elements analysed after fusion decomposition or an acid attack (Potts 1987, Table 2).

In paper II the GSF's coefficients of variation are 0.1% for Al, 0.2% for Mg, 0.6% for Ca, 0.3% for Na and 0.3% for K. The precision for the major elements is about 0.3-2% for ICP-AES with fusion and an acid attack (Jarvis & Jarvis 1992, Ramsey et al. 1995). The GSF's coefficients of variation for ICP-AES with HF-HNO<sub>3</sub>-HCl-HClO<sub>4</sub> attack (method code 311P) are < 1% for Ti, Al, Fe, Mn, Mg and Ca, and > 1% for Na, K and P (Riitta Juvonen 1995, unpublished results).

As shown in Table 2, not all the components of the total analysis of rocks and minerals can be analysed by XRF, flame AAS and ICP-AES. The analytical procedure of individual determinations is dealt with in Section 3.

### 2.3 Mineral analysis

Mineral analyses are used to classify minerals and distinguish between them, to calculate their formulae, identify them and compare separate analyses of the same mineral. Several textbooks are available on the decomposition of minerals (e.g. Sulzek & Povondra 1989, Bock 1979, Chao & Sandszolone 1992).

The chemical analysis of silicate minerals is similar to that of rocks although the samples often have to be treated individually. The components analysed depend on the number of elements the mineral contains, the purpose of the analysis and the amount of material available. The components are reported in order of importance (Hey 1973, Samchuk & Pilipenko 1987). A substantial proportion of mineral analyses are currently made as microanalyses (electron probe microanalysis and ion microprobe analysis), in which quantitative analysis on the surface of a polished thin section or the well-polished surface of a sample yields data on the concentrations of major, minor and trace elements, the accuracy of which depends on the reference and control samples available (Potts 1993).

The present author has analysed over 100 mineral samples at the GSF, the data on some of which have not been published before. The chemical analyses of 63 mineral

samples are listed in tabular form in the Appendix. The determinations were made with the modified classical methods described above, flame AAS and methods for individual determination (I-VIII). Analyses of bityite and kunzite minerals are dealt with in Papers III and IV.

#### 2.4 Analysis of special samples

Meteorites are rather difficult to analyse chemically. Preparing a representative sample tends to be a demanding task as meteorites are frequently very heterogeneous. Powdered meteorites can be analysed for many major, minor and trace element components with the classical and instrumental methods used for rock and mineral samples (Jarosewich 1966, Saikkonen 1967, Fuchs et al. 1973, Hughes & Hannaker 1978, Adler 1986, Paper III). One of the developers of the analytical procedure for chondrites (a group of stony meteorites) was the Finn, Birger Wiik (Wiik 1956, 1972). Table 3 gives the chemical analysis of the Malampaka stony meteorite, an olivine-bronzite chondrite in type, made by the present author (Graham et al. 1985). This analysis has not been published before. The determination methods were very similar to those used to analyse the Kivesvaara meteorite (Paper V).

The metallic iron of meteorites is analysed by dissolving the metal phase with mercury(II) chloride or copper(I) potassium chloride (Habashy 1961, Moss et al. 1967, Fuchs et al. 1973). Iron, nickel, cobalt and copper can be determined from the dissolved metal phase with various wet-chemical methods. In the analysis of the Malampaka meteorite, metallic nickel and cobalt were determined by flame AAS, and metallic iron with colorimetric method.

Some chondrite meteorites contain metal, silicate, sulphide and phosphide phases and other uncommon phases (Wedepohl 1978). These phases can be separated from each other with successive dissolutions and analysed for their elements after ion exchange separation (Shima 1974, Hughes & Hannaker 1978). Stony iron meteorites are often divided magnetically into metal and stone phases before analysis.

**Table 3.** Analysis of the Malampaka stony meteorite (olivine-bronzite chondrite). Analysed by the present author. Analytical methods: modified classical methods (gravimetric, titrimetric, colorimetric), atomic absorption spectrometry and other methods (see paper V and Graham et al. 1985).

Species	wt %	Elements	wt %
SiO <sub>2</sub>	35.4	Fe <sub>tot</sub>	36.3
MgO	23.6	Si	16.6
FeO	11.4	Mg	14.2
Al <sub>2</sub> O <sub>3</sub>	2.29	S	1.89
CaO	1.55	Ni	1.88
Na <sub>2</sub> O	1.00	Al	1.20
Cr <sub>2</sub> O <sub>3</sub>	0.47	Ca	1.11
MnO	0.30	Na	0.74
H <sub>2</sub> O <sup>+</sup>	0.20	Cr	0.32
P <sub>2</sub> O <sub>5</sub>	0.18	Mn	0.23
C <sub>tot</sub>	0.12	C	0.12
TiO <sub>2</sub>	0.12	K	0.08
K <sub>2</sub> O	<u>0.10</u>	Co	0.08
		P	0.08
Total stone material	76.7	Ti	0.07
		Cu	0.01
		H <sup>*</sup>	<u>0.02</u>
Fe	16.1		
Ni	1.76	Part total	84.9
Co	<u>0.08</u>	O <sup>#</sup>	15.1
Metallic grains	17.9	Total	100 %
FeS	<u>5.19</u>		
Sulphide grains	5.19	* calculated from H <sub>2</sub> O <sup>+</sup>	
Total	99.8	# calculated 100 - part total	

In the analysis of iron meteorites the metal phase and its inclusions can be treated separately (Moss et al. 1961).



Before 1969, meteorites were the only extraterrestrial material available for scientific study. After the successful Apollo flights, samples from the Moon became available to research teams. Among them was that of Birger Wiik, of which the present author was a member (Wiik 1975, 1986). The first flight, Apollo 11, was in 1969, and Finland was the first country outside the USA to obtain lunar samples for chemical analysis (Wiik & Ojanperä 1970).

### **3 ELEMENTS AND COMPONENTS REQUIRING INDIVIDUAL DETERMINATION**

#### **3.1 Determination of water**

According to the constitutional classification, the water in rocks and minerals is bound chemically and physically. The chemically bound water is constitutional water, or water of crystallization. The water of crystallization occurs in minerals as bound water or zeolite water. The physically bound water is adsorbed on mineral surfaces or constitutionally absorbed, or it occurs in fluid inclusions within the mineral (Pyper 1985). In conventional rock and mineral analyses, a distinction is made between bound water, here called water of crystallization,  $H_2O^+$ , and free water or moisture water,  $H_2O^-$ . The temperature reported in the determination is usually 105-110°C. The water liberated at this temperature is referred to as moisture water,  $H_2O^-$ ; the remainder is water of crystallization,  $H_2O^+$ . Note that the water of crystallization that may be liberated at the above temperature is calculated as moisture water. Correspondingly, the water liberated at high temperatures from fluid inclusions is calculated as water of crystallization. Total water is the sum of moisture and crystallization waters ( $H_2O_{tot} = H_2O^- + H_2O^+$ ).

Metamorphic and sedimentary rocks usually contain small amounts of elemental hydrogen that, under oxidizing analytical conditions, are converted into water and included in the water of crystallization. The hydroxide group (OH<sup>-</sup>), which occurs in several minerals such as amphiboles and micas, evaporates from the minerals on heating as water (Baur 1978).

In most of the classical and more recent methods for determining concentrations of total and crystallization waters, the sample is heated at high temperature with or without a flux. As a rule, the water is liberated from rocks without a flux if the temperature is sufficiently high, 1100°C, and the time of heating sufficiently long (Skinner et al. 1981). Some minerals, e.g. talc, topaz, staurolite, chondrodite, epidote and cordierite, need a flux and high temperature for water to evaporate (Riley 1958). Flux must also be used for the analysis of many micas and rocks rich in micas (Kutzuhisa 1991).

Concentrations of total and crystallization waters are usually determined with gravimetric, titrimetric or IRS methods. The gravimetric methods, including the classical Penfield method still in common use (see publication VI), are based on weighing the water expelled and collected from the sample on heating (Volborth 1969, DeLong 1981). Analytical methods based on Karl-Fisher titration are also frequently used (Troll & Farzaneh 1980, Westrich 1987). A number of instruments and methods based on IR detection of the water expelled from the sample on heating have been developed (Din & Jones 1978, Skinner et al. 1981).

A new infrared absorption method for rock and mineral samples is described in publication VI. To determine the total water, an air-dry powdered sample is ignited at 1100°C in a nitrogen atmosphere without a flux or with P<sub>2</sub>O<sub>5</sub>-flux. The water liberated is directed through an IR cell for measurement. The water of crystallization is determined in the same way but the sample is heated at 110°C before the measurement. The moisture water is determined at 110°C. The results have been compared with those of the Penfield method and found compatible. Similar results have been obtained from international geological reference samples. The new method has several advantages: operation is simple and unvarying; it is also faster than the old Penfield-method; the carbon dioxide liberated from samples does not interfere with the

determination; nor does fluorine cause error in the water results when the sample in the combustion boat is covered with quartz powder (Paper VI, Saikkonen 1990).

### 3.2 Determination of ferrous iron

Iron occurs in rocks and minerals in oxidation states of +II and +III and in very small amounts as native iron. Knowledge of ferrous and ferric iron concentrations is important for geochemical and petrological studies, for instance, when calculating rock norms and investigating magmatic processes. Meteorites usually contain native iron; in iron meteorites it is the main component (Mueller 1978).

For the determination of ferrous iron, the rock, mineral or special sample is usually dissolved. With the Mössbauer spectrometer the ratio of ferrous to ferric iron can be determined on a solid sample direct. However, the method needs refining, particularly for rock samples (Bancroft et al. 1977). There are far fewer methods for determining ferric than ferrous iron, and the ferric iron concentration is usually calculated as the difference between total and ferrous irons. Several methods are available for determining total iron, and the procedure is generally fairly easy. Detailed descriptions of the analytical methods for ferrous, ferric and total iron and their history have been published by Maxwell (1968) and Sulzec & Povondra (1989).

As a technical procedure, the determination of ferrous iron may be straightforward but it may still pose an awkward analytical problem. Most analytical errors arise during the preparation and decomposition of samples. Ferrous iron may be oxidized into ferric iron in the course of grinding. To prevent oxidation, the grinding should be done in an inert liquid, e.g. acetone, as this prevents air from reaching the sample and also reduces heat generation. The metallic iron in grinding vessels causes an error by reducing some of the ferric iron into ferrous iron. Such contamination can be avoided by grinding the sample in an agate mortar. Tungsten carbide, which is often used in grinders, also acts as a reductant, making the concentration of ferrous iron higher than it is in reality. If the sample is ground mechanically, the grinding time should be as

short as possible to minimize oxidation. The grain size of the sample should be about 80 mesh, i.e. less than 0.175 mm, for the sample to dissolve in acids. A good grinding vessel is one that prevents excessive heating (Rice 1982, Whipple et al. 1984, Paper VII).

Ferrous iron is easily oxidized when a sample is dissolved in acids. To prevent this, the sample should be dissolved in an inert atmosphere, e.g. oxygen-free nitrogen or carbon dioxide gas. The effect of atmospheric oxygen can be minimized by painstaking and careful work at all stages of decomposition. If a known amount of oxidant is used in decomposition to oxidize the dissolving ferrous iron into ferric iron, no inert atmosphere is needed. The oxidizing or reducing components in the sample alter the true ferrous iron/ferric iron ratio during the decomposition. These oxidizing elements include manganese (III), chromium (VI) and vanadium (V). Native iron, sulphur (II) and organic matter are reducing agents (Fritz & Popp 1985, Kane & Skeen 1993).

The weak point in acid decomposition is that some iron-bearing minerals dissolve poorly in acids; not even prolonged leach in the much-used hydrofluoric-sulphuric acid mixture can guarantee complete decomposition of the sample. Tourmaline, staurolite, ilmenite, magnetite, chromite and a number of other less common minerals do not dissolve at all, or only partially, during acid treatment. Prolonged boiling in acid easily results in the oxidation of ferrous iron, as concentrated sulphuric acid is a very effective oxidant. It might be advisable to repeat the acid decomposition and to try and dissolve the residue once again. When the author used a decomposition bomb for rock samples, a portion of ferrous iron oxidized, probably because the dissolution vessel was not tight enough. A sample can also be brought into solution with a flux such as sodium fluoroborate, lithium metaborate or lithium tetraborate. According to Kiss (1984), the constitutional oxygen in the flux may act as an oxidizer for ferrous iron.

The concentration of ferrous iron in rock and mineral samples is usually determined from dissolved sample. Exceptions to this rule are Mössbauer spectrometric measurements, which use powdered sample (Dryar et al. 1987, Fudali 1988). The concentration of ferrous iron in sample solute can be determined titrimetrically (Whipple 1974, Kiss 1977, Graff 1983), spectrometrically (Kiss 1984, Bruce & Bower 1987, Endo et al. 1992, Flock & Koch 1993) or polarographically (Beyer et al. 1975,

Moore 1979). Great care must be taken to ensure that the oxidation state of ferrous iron remains unchanged while the measuring solution is prepared and also during the measurement.

Titration of ferrous iron is undertaken as a visual or potentiometric oxidation/reduction procedure, most commonly using potassium dichromate solution as the titrant. If the sample is dissolved in the presence of an excess oxidant, the residual oxidant can be titrated with a ferrous iron solution of known strength. This solution is often titrated with a potassium dichromate solution. The concentration of ferrous iron in the sample can then be calculated from the data thus obtained.

It is still difficult to determine concentrations of ferrous iron in minerals that do not go readily into solution and in rocks containing these minerals, as there is no entirely satisfactory analytical method for that purpose. One of the most useful available for determining ferrous iron in small mineral samples is probably the micromethod introduced by Kiss. In it a mineral sample weighing a few milligrams is placed in a quartz vessel and dissolved in cerium(IV)/phosphoric acid at 325°C. The concentration of ferrous iron is then measured indirectly by potentiometric titration of the excess cerium (IV) with ferrous iron solution (Kiss 1987).

In contrast, several methods are available for the satisfactory determination of ferrous iron in readily soluble rocks and minerals. All have high enough accuracy and precision but their rapidity for the routine analysis of large series of samples could be better.

Publication VII compares three titrimetric methods making use of 13 GSF and 31 international geological reference samples. These are the method of Amonette & Scott (1991), the modified method of Wilson (Wilson 1955, Whipple 1974) and the modified method of Pratt (Jackson et al. 1987). All the methods are useful for samples that can be dissolved in acids and do not contain oxidizing or reducing components. The sulphur in acid-soluble sulphides in particular causes large errors in the method of Amonette & Scott and also in that of Wilson. In Pratt's procedure, soluble S(II) as hydrogen sulphide gas does not interfere. The modified method of Pratt is the most useful of the three for determining ferrous iron in unknown rock samples (Paper VII).

### 3.3 Determination of carbon

Carbon, which is present in rocks and minerals in concentrations ranging from several percent to a few ppm, most often occurs as a carbonate such as calcite, dolomite or siderite. The amount of other carbon-bearing material, i.e. graphite and organic carbon, is usually low, but in graphite schists the concentration of graphite carbon is commonly several percent or even tens of percent (Loukola-Ruskeeniemi 1992). Some minerals have constitutional elemental carbon or CO or CN groups (Zemann 1978). Fluid inclusions of metamorphic rocks often contain carbon dioxide and hydrocarbons as gas or liquid (Roedder 1984).

In rock and mineral analyses, carbon is most often determined as carbonate carbon (CO<sub>2</sub>) and total carbon. The concentration of non-carbonate carbon is obtained by subtracting the concentration of carbonate carbon from that of total carbon. The non-carbonate carbon is either graphite or other forms of element carbon derived from organic matter (Leventhal & Shaw 1980).

Most of the analytical methods are based on the decomposition of carbonates with acid, ignition of the sample at high temperature or wet-oxidation of carbon, and the gravimetric, titrimetric, colorimetric or IR spectrometric determination of the carbon dioxide thus generated (Paper VIII, Saikkonen 1994). The carbonate and non-carbonate carbons can be separated from each other by removing the carbonate carbon with acid decomposition. Attempts have been made to separate the carbon phases with thermal decomposition but the procedure is difficult (Charles & Simmons 1986, Saikkonen 1993).

In the study discussed in Paper VIII, total and non-carbonate carbon were determined with the IR carbon analyser, CR-12 (LECO Corporation). Before the non-carbonate carbon was measured, the carbonate carbon was removed from the sample by acid treatment. Twenty international geological reference samples and 13 GSF rock reference samples were analysed for this study. The results were highly satisfactory, particularly when compared with those reported for the 20 international reference samples. The concentrations of carbonate and non-carbonate carbons obtained for the

GSF reference samples were compatible with the gravimetric data. The precision of the results, which was about 1%, 5% or 10% with a carbon concentration of about 10%, 1% or 0.1%, respectively, was good and consistent with the trend towards a relatively low standard deviation at high concentrations but high deviation at low concentrations. Once the CR-12 instrument is set up and has stabilized, the operation is easy. It is also rapid: about 70 determinations of total carbon and 40 determinations of the non-carbonate carbon can be made by one analyst daily, compared with 10 determinations with the gravimetric method. The method is suitable for determining the carbon content of ancient sediments and of igneous and metamorphic rock samples containing more than 0.01% C. A sample size of 0.5-1.0 g is recommended.

### **3.4 Determination of halogens, sulphur and loss on ignition**

#### **Determination of halogens**

The mean concentrations of fluorine, chlorine, bromine and iodine in silicate rocks are shown in Table 4. The most common fluorine-bearing minerals are biotite, apatite and fluorite. Scapolite and sodalite are chlorine-bearing silicate minerals. Bromine is a relatively rare element, but in marine sediments with organic component and in sedimentary rocks its concentrations may exceed 100 ppm (Koljonen 1992). Iodine, the rarest of the halogens, has the highest concentrations in marine sediments and sedimentary rocks. It occurs in various minerals, most commonly as silver, copper iodides, lead iodides and calcium iodate, or lautarite, one of the most important iodine minerals in sediments (Wedepohl 1978).

The detection limits of different methods for halogens in rocks and minerals are listed in Table 5.

**Table 4.** Mean halogen concentrations (ppm) in silicate rocks (Jeffery & Hutchison 1983) and halogen concentrations in an international reference sample, MAG-1 (marine mud) (Govindaraju 1989).

	Ultra- mafic	Mafic	Inter- mediate	Granitic	Alkaline	MAG-1
Fluorine	1-20	300-500	500-1000	200-2000	500-2000	770
Chlorine	100-400	100-400	100-400	100-400	200-2000	3.1%
Bromine	0.1-2	0.1-2	0.2-2	0.5-2		252
Iodine	0.1-0.4	0.1-0.4	0.1-0.4	0.1-0.4		380

**Table 5.** Detection limits of different methods for halogens (ppm in rock). Methods: ion-specific electrode, IS; ion-chromatography, IC; XRF; neutron activation, NAA; spectrophotometry, CK; and "others", OTH. Samples were decomposed with fusion and the elements separated by pyrohydrolyse or ion-exchange chromatography. XRF determinations were made on briquetted samples.

	IS fusion a.	IC pyroh. b.	XRF briq. c.	NAA pyroh. d.	CK fusion	OTH
Fluorine	20-40	20-50	5600		10	e.
Chlorine	40-100	20-50	50	2.9	20	f. 5 g.
Bromine	0.1 h.		8	0.2	1	i. 0.0 j.
Iodine			6 k.	0.1	0.04 l.	

a. Hoffstetter et al., 1991 b. Hall et al., 1986 c. Potts, 1993 d. Langenauer et al., 1992 e. Fuge and Andrews, 1985 f. Hoffstetter et al., 1991 g. separation by distillation and ion-specific electrode, Elsheimer, 1987 h. separation by ion-exchange chromatography and ion-specific electrode, Akaiva et al., 1980 i. Pyen et al., 1980 j. mass spectrometer, Heuman et al, 1983 k. Coscrove, 1970 l. Fuge et al., 1978.



Rocks and minerals can be analysed for fluorine and chlorine with a number of methods. Normal silicate rock samples can easily be analysed with an ion-specific electrode (Fabbri & Donati 1981, Stecher 1983, Yuchi et al. 1988, Rice 1988), by ion chromatography (Conrad & Brownlee 1988, Hall et al. 1986, Kennedy et al. 1983, Wilson & Kent 1982, Ewans et al. 1981, Gent & Wilson 1985), XRF (Leoni et al. 1982, Langenauer et al. 1992) or spectrophotometry (Fuge & Andrews 1985, Adelantado et al. 1985, Hoffstetter et al. 1991). Low concentrations (<20 ppm) are more difficult to determine; the sample must be bigger, and fluorine and chlorine must be separated from the sample matrix and concentrated. Bromine and iodine can be determined by spectrophotometry (Pye et al. 1980, Fuge et al. 1978), XRF (Ullman & Tissue 1983, Croscove 1970) or activation analysis (Langenauer et al. 1992).

In Chemical Laboratory of the GSF, fluorine concentrations of rocks and minerals are determined with an ion-specific electrode from a solute produced with sodium hydroxide fusion. The corresponding chlorine determinations are made by spectrophotometry. The sample is dissolved with sodium carbonate fusion. Both methods gave satisfactory results when compared with those reported for several GSF and international reference samples (Rautiainen & Saikkonen, unpublished results).

### **Determination of sulphur**

Sulphur occurs in rocks as sulphides, sulpho-salts, sulphates, native sulphur or organic sulphur. Sulphide minerals such as pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) and pyrite ( $\text{FeS}_2$ ) are present in low abundances (0.01-0.1%) in almost all rocks. Many sulphide minerals form ores as a result of various geological processes. Sulphate minerals, the most common of which are gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), alum ( $\text{KAlSO}_4 \cdot 12 \text{H}_2\text{O}$ ) and barite ( $\text{BaSO}_4$ ), are abundant in marine sediments and sedimentary rocks. Soluble sulphates and gaseous sulphur compounds occur in mineral inclusions. Elementary sulphur is formed through

the bacterial reduction of sulphates or the oxidation of volcanic hydrogen sulphide gas. Organic sulphur compounds (e.g. S-aminoacids) are formed through sulphate reduction (Wuesch 1978).

The sulphur in rocks and minerals is determined from pulverized samples. Excessive grinding may oxidize part of the sulphides into sulphur dioxide, which is then expelled from the sample. Sulphide may oxidize into sulphate, causing an error in the concentration of sulphide sulphur in the sample.

Selective leaches are used for quantitative determinations of different sulphur forms (Rice et al. 1993). The success of the determination depends on the mineral composition and grain size of the sample, the degree of crystallization of the sulphide minerals, the concentration of ferric iron in the sample, and the degree of diagenesis or metamorphism of sediments and sedimentary rocks. The sample must, therefore, be thoroughly examined before analysis. Information on the mineral and elemental composition of the sample also facilitates performance of the analysis (Canfield et al. 1986, Tuttle et al. 1986, Jackson et al. 1987). In rock and mineral analysis, it is often sufficient to determine total sulphur ( $S_{\text{tot}}$ ) when the sulphur concentration is low,  $<0.1\%$ . If sulphate and sulphide sulphurs are measured independently, their concentrations are given as sulphur trioxide and native sulphur. In general, total sulphur is reported as native sulphur. Sulphide correction must then be made for the oxides of the analysis by subtracting the amount of oxygen corresponding to the amount of sulphur from the sum of the oxides if other elements occurring as sulphides, e.g. iron, have been reported as oxides. The correction is unnecessary if the sulphate sulphur is reported as  $\text{SO}_3$ . The sulphide correction is feasible only if information is available on the mineral composition and analytical conditions. Pyrite does not go into solution in the conventional determination of ferrous iron with the Pratt method. Therefore, the ferrous iron of pyrite is often erroneously reported in the analysis as  $\text{Fe}^{3+}$ . In the classical methods of sulphur determination, the sample is usually dissolved by fusion with sodium carbonate, and the total sulphur is oxidized into sulphate and precipitated as barium sulphate. This method is not suitable for low concentrations, as the  $\text{BaSO}_4$  precipitate may include impurities. Sample can also be heated at a high temperature in oxygen or air flux, often in the presence of an oxidant. Sulphur is then oxidized into sulphur dioxide and trioxide. The gases are absorbed into a suitable

solution and the sulphur oxides determined spectrophotometrically, gravimetrically or titrimetrically (Johnson & Maxwell 1981).

The sulphur concentration of rocks and minerals is usually measured with more or less automated analysers. An X-ray fluorescence spectrometer is useful for the rapid determination of several elements simultaneously. The powdered sample to be analysed is compressed into a briquette or converted into a glass-like fusion prepriate. For the briquette, the detection limit of sulphur in routine determinations is about 20 ppm (Potts 1993). The disadvantage of this prepriate is that correct sulphur data cannot be obtained unless the sample and standard sample are of similar sulphide mineral composition (Leoni et al. 1982). When measured on the fusion prepriate, the detection limit of sulphur is about 120 ppm (Potts 1993).

In many analytical methods, sulphur is first separated by heating the sample under oxidizing conditions. Sulphur oxidized into sulphur dioxide in pyrolysis can be determined by IR spectrometry (Terashima 1988), ion chromatography (Hall et al. 1986) and iodometric (Bouvier et al. 1972) or colorimetric titration (Atkin & Somerfield 1994). Hall and Vaive (1989) have compared the sulphur determination methods used by the Geological Survey of Canada, that is, pyrohydrolyse-ion chromatography, pyrolyse-infra-red spectrometry and pyrolyse-titration.

### **Determination of loss on ignition**

The reduction in the mass of the sample on ignition is reported as loss on ignition (LOI). On ignition (usually for 1 h at 1000°C), water together with carbon in its various forms is expelled from the weighed sample as are, either totally or partially, sulphur, fluorine, chlorine and such rare elements as mercury and selenium. However, the mass also increases during ignition, as ferrous oxide is oxidized into ferric oxide. The mass increment can be calculated if the concentration of ferrous iron is known. If it is not, then total iron must be reported as  $\text{Fe}_2\text{O}_3$ ; the plus error due to the expression

of ferrous iron as ferric iron is then of the same magnitude as the minus error in the weighed LOI. Thus the errors compensate for each other and do not affect the sum of the oxides in total analysis. The determination of LOI complements the total rock analysis. Measurement of the concentrations of volatile components expelled from the sample on ignition can be used to test the accuracy of rock analyses by XRF and plasma spectrometry if it is neither possible nor necessary to determine these concentrations independently (Lechler & Desilets 1987, King & Vivit 1988, Huka & Rubeska 1993, Kane & Skeen 1993).

#### 4 SUMMARY

This study investigated and developed chemical analytical methods for rocks, minerals and other geological samples such as meteorites. With the aid of Finnish and international geological reference samples the methods were compared with other methods in use. Numerous rock, mineral, meteorite and other geological samples were analysed with modified and classical wet-chemical and instrumental methods. The results are presented in papers I-VIII.

The analytical method comprising modified old and new determination methods used for this work is one of the most accurate available for the total analysis of many geological samples. Normally the following major and minor components are determined in total analysis: silica, titanium oxide, aluminium oxide, manganese oxide, ferric iron oxide, ferrous iron oxide, calcium oxide, magnesium oxide, constitutional water ( $H_2O^+$ ) and moisture water ( $H_2O^-$ ) and often also fluorine, chlorine, sulphur and native carbon. In the main-portion analysis of the method, silica, calcium oxide and magnesium oxide as well as the oxide-group precipitate of all the elements that precipitate with ammonia are determined gravimetrically. Titanium oxide and total iron(III)oxide are measured from the oxide group precipitate spectro- photometrically. Aluminium oxide is obtained by subtracting the weight of the other oxides from the total weight of the oxide group precipitate. The main-portion analysis was tested and investigated in publication II.

The second subsample in the total analysis method is dissolved with hydrofluoric, nitric and perchloric acids. Sodium and potassium are determined from the solute thus obtained by flame photometry or flame AAS. Manganese and phosphorus concentrations are measured colorimetrically as permanganate and molybdo-vanado phosphoric acid complex (Fig. 1). Water, ferrous iron and carbon dioxide, and often also native carbon, fluorine, chlorine and sulphur, are analysed as individual determinations. The concentrations of total and constitutional waters in the sample are determined with IR spectrometry. The water of crystallization in the sample can also be obtained by subtracting the concentration of moisture water from that of total water. The concentration of ferric iron is calculated by subtracting that of ferrous iron from total iron (Fig. 1).

The above package of methods is suitable for analysing single samples requiring an individual approach and analysis, e.g. rock and mineral reference samples, certain mineral samples and meteorite samples. It cannot be used for analysing samples en masse. Instruments suitable for this purpose are the X-ray fluorescence spectrometer, atomic absorption spectrophotometer and plasma spectrometer. The precision and accuracy of the analyses of many of the elements determined with XRF, that is, Si, Ti, Al, Fe<sub>tot</sub>, Mn, Mg, Ca, Na, K and P, are of the same order of magnitude as those determined in total analysis as described above. The accuracies of flame AAS and ICP-AES analyses are equal to those of XRF for some elements. Many trace elements can also be determined with XRF, AAS and ICP-AES instruments. But, as pointed out above, in the total analysis of rocks and minerals by these instruments cannot analyse all of the components (Table 2). For individual determinations a new subsample must be taken from the sample powder, which then requires separate chemical pretreatment (dissolution, separation, etc.) and measurement of concentration.

The objectives of the present work were to develop new and more rapid individual determination methods that would be appropriate in other respects, too (e.g. accuracy, precision and detection limit) for analysing rocks, minerals and other related geological samples, and to improve existing methods for individual determination.

The method for determining water with IR absorption was investigated and refined in the course of the work. It has several advantages. Operation with the RMC-100

instrument is simple and unvarying. The total and crystallization waters of rocks and minerals can clearly be determined more rapidly with this method than with the gravimetric Penfield method and with equally good accuracy. This method is in use at the chemical laboratory of GSF (Paper VI, Saikkonen 1990).

The analytical methods for ferrous iron were assessed by comparing three titrimetric methods: the Pratt method, the Wilson method and the Amonette & Scott method. It was concluded that the modified Pratt method is the most useful for determining of ferrous iron in unknown samples. The Wilson method and the Amonette & Scott method can be applied to samples of known mineral composition. The modified Pratt method is in use at the chemical laboratory of GSF (Paper VII).

The method based on IR absorption and used for determining total carbon in geological samples was studied and an IR method was developed for determining the concentration of non-carbonate carbon, which is either graphite or other forms of element carbon deriving from organic matter. The concentration of carbonate carbon is obtained by subtracting the concentration of non-carbonate carbon from that of total carbon. The methods described above are in use at the chemical laboratory of GSF (Paper VIII).

Methods for determining halogens, sulphur and LOI were reviewed on the basis of the literature and in the light of practical experience.

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# Appendix

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>	H <sub>2</sub> O*	H <sub>2</sub> O*	F	Cl	S	Li <sub>2</sub> O	Rb <sub>2</sub> O	Cs <sub>2</sub> O	BeO	SrO	BaO	Cr <sub>2</sub> O <sub>3</sub>	NiO	B <sub>2</sub> O <sub>3</sub>	LOI	Total		
<b>Silicates</b>																														
40. Turmalin	36.19	0.27	36.77	8.96 <sub>i</sub>		0.14	4.69	0.22	1.64	0.06	0.00	0.00	2.59	0.03	0.15												8.78		100.44	
41. Turmalin	35.25	0.27	35.28	13.26 <sub>i</sub>		0.20	2.52	0.09	1.66	0.06	0.00	0.00	2.61	0.11	0.35												9.16		100.72	
42. Turmalin	35.26	0.22	37.99	10.94 <sub>i</sub>		0.25	0.62	0.10	1.96	0.06	0.00	0.00	2.84	0.04	0.97												8.90		100.33	
43. Turmalin	35.73	0.10	38.83	7.15 <sub>i</sub>		1.08	0.37	0.19	2.26	0.06	0.00	0.00	2.74	0.04	1.18												9.03		99.54	
44. Turmalin	36.82	0.92	32.27	2.59 <sub>i</sub>		0.14	11.03	1.51	1.74	0.06	0.00	0.00	2.60	0.04	0.53												8.22		98.30	
45. Turmalin	36.85	0.02	43.21	0.23 <sub>i</sub>		1.26	0.12	0.38	1.74	0.18	0.00	0.00	3.06	0.08	1.04												10.12		99.67	
46. Turmalin	38.38	0.03	41.91	0.40 <sub>i</sub>		0.41	0.43	0.14	1.76	0.45	0.00	0.00	3.22	0.09	0.93												9.77		99.39	
47. Vermiculite	38.14	1.53	16.59	0.30	0.11	0.01	23.09	1.47	0.33	0.15	0.03	0.00	10.41	7.56	1.60														100.65	
48. Zoisite (Tanzanite)	39.99	0.05	34.24	0.06 <sub>i</sub>		0.04	0.04	24.40	0.09	0.06	0.07	0.00	1.15	0.01	0.02														100.49	
<b>Oxides</b>																														
49. Brokite			0.32	0.63 <sub>i</sub>		0.01	0.10																							0.11
50. Rutile			0.32	1.52 <sub>i</sub>		0.03	0.07																							0.01
<b>Phosphates</b>																														
51. Amplygonite	0.14	0.00	34.70	0.00	0.00	0.00	0.00	0.01	0.29	0.02	48.5		2.80	0.00	7.24															100.32
52. Apatite				1.11 <sub>i</sub>		0.04	0.77	54.0	0.17	0.03	42.9				0.68								0.48				0.00			100.2
53. Apatite				0.43 <sub>i</sub>		0.02	0.50	53.8	0.13	0.02	42.3				0.41								0.42				0.00			98.6
54. Apatite				0.53 <sub>i</sub>		0.03	0.57	53.7	0.22	0.07	42.7				0.73								0.55				0.00			99.1
55. Apatite				0.36 <sub>i</sub>		0.01	0.03	55.2	0.14	0.03	42.9				1.00								0.72				0.00			100.4
56. Apatite				0.66 <sub>i</sub>		0.02	0.34	54.3	0.16	0.03	42.3				0.76								0.70				0.00			99.3
57. Apatite				1.56 <sub>i</sub>		0.07	0.19	53.7	0.17	0.01	41.2				0.79								0.55				0.00			98.2
58. Apatite	1.43		0.23	1.05 <sub>i</sub>		0.69		51.96	0.76	0.06	38.71	0.19	1.04	0.18	2.43	0.00	0.02					0.32	0.00						98.5	
59. Eosphorite	0.16	0.00	24.50	0.22	1.98	24.30	0.00	0.06	0.15	0.02	32.95		14.26	0.02	0.41															99.82
60. Herderite	0.40		0.19	0.17 <sub>i</sub>		0.29		36.24	0.77	0.08	43.21		3.28	0.00	4.21									14.81		0.30				100.85
61. Triflylite- lithiophilite	0.12	0.01	0.08	0.48	29.37	13.39	0.68	0.06	0.07	0.03	45.99	0.00	0.02	0.02																98.83
62. Triplite	0.00	0.12	0.16	0.43	15.47	44.55	0.10	0.37	0.00	0.02	32.39	0.00	0.88	0.00	8.00															99.26
<b>Sulfates</b>																														
63. Selestine								0.83																						99.29

t = total

Numbers stored in the database of GSF (Gustafsson & Saikkonen 1994) (in Finnish):

1. 71001, 2. 71002, 3. 71003, 4. 71004, 5. 72101, 6. 72102, 7. 840003, 8. 79030, 9. 72089, 10. 72090, 11. 74126, 12. 74127, 13. 840005, 14. 67039, 19. 81021, 20. 71022, 21. 71023, 22. 71076, 23. 71077, 24. 77383, 25. 840004, 26. 78187, 27. 72088, 40. 73005, 41. 73006, 42. 73007, 43. 73008, 44. 73009, 45. 73010, 46. 73011, 47. 840001, 48. 840002, 49. 71051, 50. 71050, 51. 76152, 52. 80025, 53. 80026, 54. 80027, 55. 80028, 56. 80029, 57. 80030, 58. 81020, 59. 76112, 60. 81022, 61. 75124, 62. 76098, 63. 69132.

About 100 mineral samples, in which 1-5 elements or constituents have been analysed by the present author, are albites, allanites, antigorites, apatites, biotites, britolites, calsites, chromites, chrysotiles, cordierites, cryolites, hematites, hornblendes, kornerubines, kyanites, ilmenites, kaolinites, lepidolites, margarites, microclines, plagioclases, pyrites, quartzes, siderites, spodumenes, talcs, topases, and zeolites.





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