

ANALYTICAL TECHNIQUES FOR ELEMENTAL ANALYSIS OF MINERALS

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Summary

Performing elemental analysis of minerals is one of the most important routine works in Earth sciences. Among the numerous analytical techniques for elemental analysis, beam methods (especially electron microprobe analysis) are the most common and important methods. Further improvements of the technical equipment and adjacent software modules of these methods guarantee their continuous outstanding importance in Earth science research work.

1. Introduction

Elemental analysis of minerals is one of the most important routine working methods in Earth sciences, since information on the elemental composition of minerals gives access to a variety of genetic parameters of minerals (for example, changes of chemical environment during mineral growth) and rocks (for example, pressure–temperature path determination), which are of fundamental importance to the understanding of geological processes.

Besides these scientific applications, elemental analyses of minerals (and mineral concentrates) are of economic importance, since many minerals are used in industry (for example, quartz as a raw material in the silicon industry, talc as an additive in pharmaceutical products), where elemental analyses of such minerals for quality assurance are required.

Choosing an appropriate technique for elemental analysis of minerals is not always an easy task, since several parameters which depend on the sample and the analytical requirements have to be considered. However, in order to limit this article to a discussion of the most commonly used analytical methods, some general information about the elemental composition of minerals is presented first.

Looking at Table 1, which shows the elemental distribution of Earth's crust for the most common 20 elements in weight percent (which represent 99.59% of the total), it is no surprise that the most common minerals of Earth's crust (which are known as "rock-forming minerals") are mostly oxygen-containing phases (Table 2).

1.	Oxygen	46.60 %	11.	Phosphorus	0.10 %
2.	Silicon	27.72 %	12.	Manganese	0.09 %
3.	Alumina	8.13 %	13.	Fluorine	0.06 %
4.	Iron	5.00 %	14.	Barium	0.04 %
5.	Calcium	3.63 %	15.	Strontium	0.04 %
6.	Sodium	2.83 %	16.	Sulphur	0.03 %
7.	Potassium	2.59 %	17.	Carbon	0.02 %
8.	Magnesium	2.09 %	18.	Zirconium	0.02 %
9.	Titanium	0.44 %	19.	Vanadium	0.01 %
10.	Hydrogen	0.14 %	20.	Chlorine	0.01 %

Table 1. Distribution of elements in Earth's crust in weight percent

ca. 58.0 %	Feldspars	
	Orthoclase	$KAlSi_3O_8$
	Albite	$NaAlSi_3O_8$
	Anorthite	$Ca_2Al_2Si_2O_6$
ca. 16.5 %	Pyroxenes (e.g. diopside)	$(Ca,Mg,Fe)_2Si_2O_6$
	Amphiboles (e.g. hornblende)	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
	Olivines (e.g. forsterite, fayalite)	$(Mg,Fe)_2SiO_4$
ca. 12.5 %	Quartz	SiO_2
ca. 3.5 %	Micas (e.g. biotite)	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$
ca. 3.5 %	Magnetite	Fe_3O_4
	Hematite	Fe_2O_3
ca. 1.5 %	Calcite	$CaCO_3$
ca. 1.0 %	Clay minerals (e.g. kaolinite)	$Al_4Si_4O_{10}(OH)_8$

Table 2. Distribution of minerals in Earth's crust in volume percent

Following a broad mineral classification scheme (elements–sulfides–sulfosalts–oxides–halides–carbonates–nitrates–borates–phosphates–sulfates–tungstates–silicates), Table 2 clearly shows the dominance of minerals (about 96.5%) that belong to the mineral group of the silicates. Therefore it is obvious to concentrate in this article on the elemental analysis of silicate minerals. Major elements (above 0.1%) in the silicate group are oxygen (O), silica (Si), aluminum (Al), sodium (Na), potassium (K), calcium (Ca), iron (Fe) and magnesium (Mg). Minor elements (0.01% to 1%) and trace elements (below 0.01%) in common silicates are hydrogen (H), lithium (Li), beryllium (Be), boron (B), carbon (C), fluorine (F), phosphorus (P), sulfur (S), chlorine (Cl), titanium (Ti), chromium (Cr), manganese (Mn), nickel (Ni), zinc (Zn), zirconium (Zr), rare earth elements (REE), and so on. They may also occur as major elemental components (for example, beryllium in beryl— $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$, fluorine in topaz— $\text{Al}_2\text{F}_2\text{SiO}_4$, zirconium in zircon— ZrSiO_4).

However, as can be seen from Table 3 it is common use to present a mineral analysis not in element weight percent but as oxide weight percent, so that other mineral groups such as carbonates (for example, calcite is expressed as CaO and CO_2), sulfosalts (for example, gypsum is listed as $\text{CaO} + \text{SO}_3 + \text{H}_2\text{O}$) and oxides fit in the analysis presentation scheme of oxygen compounds. In contrast, mineral analyses of non-oxygen containing phases (for example, sulfides or halides) are presented as element weight percent.

Furthermore, Table 3 demonstrates various problems that arise in the elemental analysis of minerals, especially when using the most widely available analytical technique for that purpose, the electron microprobe (electron microprobe analysis, or EMPA). Anticipating the disadvantages of this (and other) techniques, which may cause an analyst to choose other analytical methods, and in order to discuss general problems in the elemental analysis of minerals, the most important limitations are:

- a) The inability to measure hydrogen. This is one of the most limiting factors, since many minerals (chlorites, micas, clay minerals, amphiboles, and so on) contain appreciable amounts of OH groups or H_2O .
- b) The inability to measure, or very limited possibility of measuring, the light elements (atomic number < 6) lithium, beryllium, and boron. This problem appears when dealing with minerals like spodumene (Li-pyroxene— $\text{LiAlSi}_2\text{O}_6$), beryl (Be-silicate— $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$) or minerals from the tourmaline group (B-silicates— $(\text{Na,Ca})(\text{Mg,Fe,Al,Li})(\text{OH})_4(\text{BO}_3)_3\text{Si}_6\text{O}_{18}$).
- c) The inability to determine, or very limited possibility of determining, the oxidation state of the element. Although the determination of the oxidation state of an element in a mineral is not a problem of elemental analysis in a strict sense, it is important in mineral analysis when determining site occupancies and oxidation state, especially in iron-bearing minerals (for example, Fe^{2+} content in garnet: almandine molecule— $\text{Fe}_3^{2+}\text{Al}_2(\text{SiO}_4)_3$, Fe^{3+} content in garnet: andradite molecule— $\text{Ca}_3\text{Fe}_2^{3+}(\text{SiO}_4)_3$).
- d) The detection limits are about 0.01 weight% (100 ppm) or higher for most elements. This is a limiting factor in EMPA routine analysis when analyzing trace element contents in the ppm or even sub-ppm region.

	Feldspar	Pyroxene	Garnet	Amphibole	Mica	Chlorite	Tourmaline
SiO ₂	68.49	52.94	38.68	37.66	49.17	27.54	36.13
TiO ₂	0.00	0.08	0.13	0.03	4.27	0.02	0.24
Al ₂ O ₃	19.32	5.81	20.60	20.37	31.90	22.15	30.64
FeO*	0.05	3.76	14.33	13.63	0.91	12.73	5.50
Fe ₂ O ₃ **	—	0.28	0.16	—	—	—	—
Cr ₂ O ₃	0.01	0.28	2.31	n.d.	0.02	0.01	0.05
MgO	0.02	12.89	3.95	10.85	2.29	25.43	8.82
MnO	0.00	0.04	0.53	0.19	0.03	0.00	0.00
CaO	0.10	21.98	19.23	11.96	0.05	0.09	0.51
K ₂ O	0.17	0.00	n.d.	0.74	9.59	0.04	0.10
Na ₂ O	11.65	1.82	n.d.	3.21	0.68	0.01	2.44
Total	99.81	99.88	99.92	98.64	95.01	88.02	84.43

Table 3. Examples of electron microprobe analyses of silicate minerals from crystalline basement rocks, such as metacarbonates, mica-shists, orthogneisses and amphibolites of the Oetztal–Stubai complex, Northern Tyrol, Austria

A careful review of Table 3 illustrates all four points (a–d) stated above:

- a) As can be seen there is no OH or H₂O analysis included in the table. The first three minerals (feldspar, pyroxene, and garnet) are almost OH/H₂O-free, therefore the total sum of these analyses approaches 100%. The difference from 100% may be a result of nonanalyzed minor elements such as Ba in feldspars or Zr in garnet, or to analytical precision of the method (0.2 to 0.5% relative standard deviation is possible with modern equipment for major elements). Analyses of amphibole, mica, and chlorite differ by about 1.5, 5, and 12% respectively from a 100% total. The major reason for these differences is the OH/H₂O content of these minerals. Generally amphiboles have about 1–2 wt.%, micas 4–6 wt.% and chlorites about 12 wt.% H₂O. The possibility of the omission of nonanalyzed elements such as fluorine and chlorine, which may substitute for OH in these minerals, may also account for a difference of up to several wt.%.
- b) The tourmaline analysis differs by about 15.5% from 100%. One reason is the amount of water, which is between 2–4 wt.% in tourmalines. The second reason may again come from the omission of nonanalyzed elements such as fluorine, which may account for about 1 wt.% in this mineral. However, in this example the major difficulty with electron microprobe analysis is its inability to measure the element boron, B (and also lithium, Li), which amount to about 10 wt.% B₂O₃ in tourmalines. (Note: B and Be are becoming more routine with newer electron microprobe instruments, though Li remains undetectable.)
- c) FeO* in Table 3 indicates that all the measured iron is expressed as FeO. For two analyses (pyroxene and garnet), minor contents of Fe₂O₃ are given. Measuring the oxidation state of an element with an electron microprobe is an impracticable task. Fe₂O₃** indicates calculated contents of iron in the Fe³⁺-state, using calculation schemes for chemical formulas based on stoichiometry and charge balance considerations.

- d) All the analyses in Table 3 are given to a hundredth of a weight percent. This demonstrates the detection limits of about 0.01% or higher for electron microprobe analysis. In mineral analysis it is also usual to give an undetected amount as 0.00% or “n.d.,” not detected (for example, K₂O in pyroxene or garnet analysis from Table 3). The abbreviation “n.a.” means not analyzed; the same is true of the symbol “—” (for example, Na₂O in garnet analysis from Table 3 or the various Fe₂O₃** contents in Table 3).

An additional problem in elemental analysis of minerals is caused by the mineral samples themselves: minerals are rock compounds with a small grain size, generally ranging from a micrometer ($1\mu = 10^{-3}$ mm) to a few millimeters (mm). In rare cases minerals exhibit grain sizes outside this range. Therefore one of the most widely used qualitative “analytical instruments” in mineralogy and petrology is the light microscope (polarizing transmission- or reflected-light microscopy), which can easily image grains on a micrometer scale. Furthermore, quantitative analytical techniques that can be performed at the micrometer scale are preferred.

Even when minerals have larger sizes so that sample amounts of 50 mg or even grams are available, there is another problem to consider: such “bulk samples” may contain abundant inclusions of other minerals, which can result in a systematic error in mineral separate analysis (for example, high Zr content in various silicate minerals caused by inclusions of the mineral zircon, ZrSiO₄).

Analytical methods for elemental analysis of minerals may be divided into two groups: one group of methods that uses material from separated minerals (mineral concentrates), and one group of methods where it is possible to analyze a mineral *in situ* within a rock. While the first group of methods are non-position-sensitive (bulk methods), methods in the second group are position-sensitive, since a focused beam is placed on a defined position on a mineral (beam methods).

Table 4 gives a brief overview of the detection limits of the most commonly used methods for elemental analysis in minerals. The data have to be read with caution, since some methods (marked with an asterisk) need the sample in a liquid state, so that the data have to be multiplied by the dilution factor of the corresponding sample preparation (decomposition) method.

Table 4. Brief overview on the detection limits of the most commonly used methods for elemental analysis in minerals. Some methods (marked with an asterisk) need the sample in a liquid state so that the data have to be multiplied by the dilution factor of the corresponding sample preparation (decomposition) method.

Gravimetry	0.01% to low %
Volumetry	0.01% to low %
Colorometry	0.01% to low %
AAS-flame*	0.0001%-region
AAS-graphite tube*	0.000001%-region
AAS-hydride method*	0.000001%-region
ICP-AES*	0.0001% to 0.000001%-region

XRFA	0.0001%-region
NAA	0.0001% to 0.000001%-region
MS	0.0001% to 0.000001%-region
SIMS	0.0001% to 0.000001%-region
LA-ICP-AES/LA-ICP-MS	0.0001% to 0.000001%-region
PIXE/PIGE	0.0001%-region
EMPA	0.1 to 0.01 %

Table 4. Brief overview on the detection limits of the most commonly used methods for elemental analysis in minerals. Some methods (marked with an asterisk) need the sample in a liquid state so that the data have to be multiplied by the dilution factor of the corresponding sample preparation (decomposition) method.

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Biographical Sketch

Richard Tessadri was born in 1954, in Breitenwang, Reutte-Tyrol, Austria. He studied Earth Sciences at the University of Innsbruck from 1975–1981, gaining a Ph.D. From 1982–1985 he was a university assistant at the Institute of Mineralogy and Petrography, University of Innsbruck, obtaining a research

grant from the Austrian Science Foundation, FWF, to study polymetamorphism in the Oetztal-Stubai-Complex, Austria. From 1985–1992 he was a Lecturer at the Institute of Mineralogy and Petrography where he also managed the X-Ray Laboratory and Atomic Spectroscopy Laboratory, and since 1992 he has again been a university assistant at the Institute of Mineralogy and Petrography. His teaching and research subjects cover X-ray diffraction, X-ray fluorescence, atomic absorption/emission spectroscopy, and use of the electron microprobe). He has carried out analytical work for various industries, such as industrial applications for trace element chemistry in biochemical products, and work for the paper industry and grinding tool industry.

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