15 - Lecture notes for GEOL3010

Chemical Compositions - One of the aims of elemental / chemical analysis is to calculate a structural formula and determine the distribution of cations amongst several structural sites. The process of converting chemical analysis to structural formulas is known a chemical re-calculation.

Types of elemental analysis. The choice of type of elemental analysis depends upon the concentration of the elements in the sample, the level of accuracy required, and availability of analytical equipment.

Accuracy and precision are also dependent upon the "skill" of the analyst.

What one chooses to analyze is the most important decision. The purity of the sample is an important factor. There are several methods to high grade or beneficiate samples, such that you can be assured that the sample analysis is for a single mineral.

These techniques include:

- Size fractionation
- Magnetic separation
- Density separation
- Selective dissolution treatments
- Small scale sampling

A common reference:

Physical methods in determinative mineralogy (1977) ed. J. Zussman, Academic Press, London.

Methods for elemental analysis

Dissolution methods - These methods involve dissolving the entire sample and then analyzing the concentration of dissolved ions. Concentrations can be measured with instruments such as:

- Atomic Absorption (AA)
- Electrodes
- Ion Chromatograph
- Induction Couple Plasma (ICP)

Pros - allows accurate analysis of lighter elements,

Cons - Must be a good chemist. (Often dealing with dilute solutions or one must dilution solutions, which propagates error).

X-ray methods - Two types: Energy Dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS). The latter method includes the better-known method of X-ray Fluorescence XRF. (see page 325 textbook)

EDS - the sample is the target, and the intensity of the characteristic radiation for each atom type is proportional to its abundance.

XRF - Uses Bragg's Law (n λ = 2 d sin Θ). By using crystals with known d-spacings, it is possible to analyze for a specific wavelength or energy that is characteristic of an element (e.g., λ = 1.937Å for FeK_α). The energy of the diffracted beam is proportional to the number of atoms present.
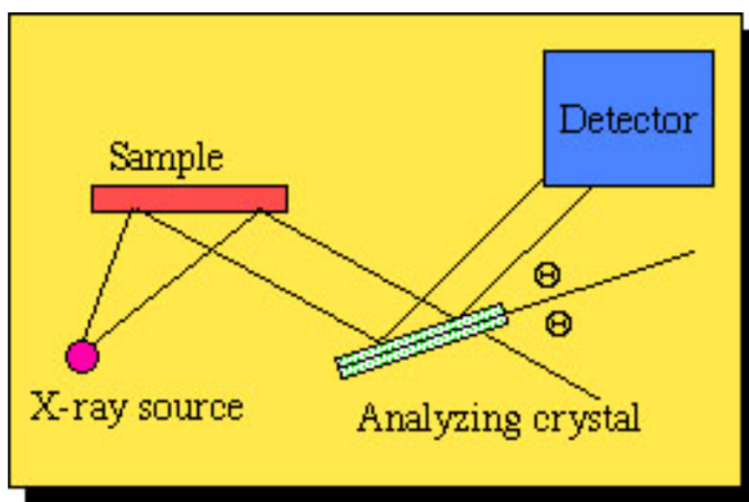
One can also excite X-rays with high energy electron source (as in the Electron Microprobe). Small sampling areas (10 microns) are possible.

Pros - Quick, relatively easy

Cons - Light elements are not amenable (H, Li, B, C, O)

Spectroscopic methods including:

FTIR, NMR, Mossbauer, Optical.

Pros - provide additional information only for particular elements and/or functional groups and coordination state.

Cons - limited access and very specific to elements and/or functional groups

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Recalculation of chemical analysis

One goal of elemental analysis is to obtain the chemical formula of a mineral. Therefore, we need to obtain the atomic proportions of the elements present.

Probably the most important aspect of quantitative elemental analysis is to make sure the total of the individual measures add up to 100%!

For the case of native elements, the measurement is simple. For example, Cu = 100%. Therefore, the intensity measurement from an XRF analysis can be made directly proportional to the amount of Cu present.

For polyatomic minerals the situation is a little more complex. Quantitative analysis requires calibration.

Let's first start by working the recalculation problem 'backwards". In other words, let's calculate the elemental weight percent of a compound from the atomic weights. We'll use halite in the example.

We know that there is one sodium atom for each chlorine atom in halite.

Given the atomic weights of Na = 22.9898 and Cl = 35.453, it is easy to show the relative weight percent of each element in the compound.

$$Wt\%Cl = \frac{35.453}{22.9898 + 35.453} = 60.1\%$$

$$Wt\%Na = \frac{22.9898}{22.9898 + 35.453} = 39.9\%$$

For a recalculation (*i.e.,* working the problem "forward") the general rule is to normalize the chemical formula by the dominant anionic group(s) (Cl^- in the case for halite and $O^=$ in the case of the rock forming silicates). Assuming there is some way to measure the weight percent of Na and Cl in halite, we can recalculate the atomic ratios. As seen in the table below the second column contains the measured values (Note that they don't add up to exactly 100%) The atomic proportions are determined by dividing the wt.% by the atomic weight. Normalization by the number of anions yields the atomic ratios, which are the subscript coefficients in the chemical formula. The resultant formula is $Na_{0.995}Cl_{1.000}$. Errors cause small problems, however upon rounding off the numbers, one can see the final formula is reported as NaCl.

Element	Weight %	Atomic weight	Atomic Proportions	Atomic Ratios
Na	39.21	22.9898	1.706	0.995
Cl	60.83	35.4530	1.715	1.000
Total	100.04	$Na_{0.995}Cl_{1.000}$		

Calculation of unit cell contents

It can be shown that the density of mineral is related to the mass of the atoms and number of atoms in the unit cell. This relation is given by the following equation.

$$D = \frac{Z \times M}{N \times V \times 10^{-24}}$$

where, D = density g/cm^3

Z = number of formula units (atoms / unit cell)

M = Molecular weight (a.m.u or g/mole)

N = Avogadro's number = 6.022 x 10^{23} (atoms/mole)

V = Volume of unit cell Å^3

10^{-24} = Å^3 --> cm^3

Dimensional analysis:

$$\frac{g}{cm^3} = \frac{\frac{atoms}{unit\ cell} \times \frac{g}{mole}}{\frac{atoms}{mole} \times \frac{Å^3}{unit\ cell} \times 10^{-24} \frac{cm^3}{Å^3}}$$

We can rearrange the equation in terms of the total mass of the unit cell,

$$Z \ x \ M = N \ x \ D \ x \ V \ x \ 10^{-24}$$

or

$$Z = \frac{0.6022 \times D \times V}{M}$$

The amount of each constituent (Q) (*i.e.*, element or oxide) is usually given as a fraction (q) of the total mineral. That is, every 100 a.m.u. of mineral contains q a.m.u. of Q or q/M atoms of Q. Therefore, by simple proportion the number of Q atoms in the unit cell is,

$$Z = \frac{0.6022 \times D \times V \times q}{M}$$

Best shown by example -

Halite

D =2.16 g/cm^3 , a = 5.65Å, V = 179.4Å^3, q_{Na} = 0.3931, M_{Na} = 22.9898 g

$$Z = \frac{0.6022 \times 2.16 \times 179.4 \times 0.3931}{22.9898} = 3.98$$

Unit cell of halite is Na_4Cl_4

Quartz

D =2.65 g/cm^3 , V = 113, q_{Na} = 0.466, M_{Si} = 28.086g

$$Z = \frac{0.6022 \times 2.65 \times 113 \times 0.466}{28.086} = 2.992$$

By difference the percentage of oxygen = 53.2%, M = 15.9994

$$Z = \frac{0.6022 \times 2.65 \times 113 \times 0.532}{15.9994} = 5.996$$

Unit cell of quartz is Si_3O_6