BRUKER

Mining

Sample

LYNXEYE detector

D4 ENDEAVOR

Result

Quantitative Analysis of Geological Samples: Combined XRD-XRF Analysis

Introduction

XRD and XRF are highly complementary materials analysis methods which, when used together, greatly improve the accuracy of phase identification and quantitative analysis. The combination of both methods provides an increase in the numbers of measured parameters, which means that fewer assumptions are needed for analysis. This in turn provides not only greater accuracy of results, but also increases the range of samples that can be measured to include samples about which little or nothing is known in advance.

XRD is the most direct and accurate analytical method for determining the presence and absolute amounts of mineral species in a sample. Ambiguous results may be obtained however, if the sample chemistry and/or origin are unknown. In these cases phase identification can be difficult; in particular, isostructural phases with similar chemical composition will give similar powder diffraction patterns.

In contrast to XRD, XRF provides highly accurate information about the elemental composition of a sample, but it cannot deliver direct phase information. Mass-balance calculations may give sufficient phase information in some cases, but can also lead to meaningless results e.g. in the presence of polymorphs.

It is the complimentary nature of the XRD and XRF methods which makes them a valuable tool for quantitative phase analysis in numerous applications ranging from scientific research to industrial high-throughput quality control. Particularily in mineralogical and geological application areas, the combined use of XRD and XRF is booming, offering completely new insights into materials and processes. Typical examples are the cement, minerals & mining, and industrial minerals industries, where the quality of products and / or efficiency of processes is governed by both phase and elemental composition. The combined use of XRD and XRF methods allows the reliable analysis of materials, for which the individual methods fail to deliver accurate and reliable results.

Quantitative phase and element analysis of host/waste rocks and tailings is an important application in the minerals and mining industry with respect to both process optimization (e.g. acid leaching) and environmental protection: Mining and milling operations are responsible for the production of billions of tonnes of waste rock and finely crushed tailings worldwide. An important application is the knowledge of the relative amounts of the minerals with acid-producing or neutralization potential for successful acid-base accounting with respect to both the leaching process as well as acid mine drainage, with its detrimental effects on environment.

As an example, we report combined XRD-XRF analysis of an intrusive rock with unknown composition. Of particular interest was its classification by mineral content as well as the detection and accurate quantification of potentially present minerals with significant acid-producing or neutralization potential.

Powder diffraction data were recorded using a D4 ENDEAVOR powder diffractometer equipped with a LYNXEYE^{TM} detector (Fig. 1); the total measurement time required was about 5 minutes. For phase identification and quantification, the DIFFRAC^{plus} software packages EVA, SEARCH and TOPAS were used. Standardless XRF measurements on the same sample were performed with the S4 PIONEER and the SPECTRA^{plus} software (Fig. 1).

1) Phase identification

Fig. 2 and Tab. 1 show the XRD powder data and the phase identification results. The major rock forming minerals plagioclase, quartz, diopside and muscovite are easily and correctly identified in a single default run. Note, that the highly sensitive SEARCH algorithm clearly prefers albite (Na-plagioclase) versus anorthite (Ca-plagioclase) as a result of the slightly different lattice parameters of both plagioclase solid solution end members. Best SEARCH figure-of-merits obtained for the individual phases were 0.65 and 1.48, respectively. Neither ore minerals nor any K-feldspars or feldspathoids could be detected.
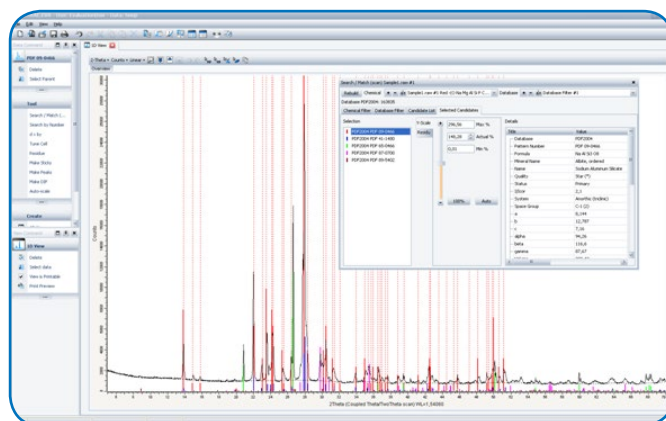

Fig. 2: EVA phase identification results.

Tab. 1: EVA phase identification results.

SS-VVV-PPPP	Compound Name
00-009-0466 (*)	Albite
00-041-1480 (I)	Albite, calcian
03-065-0466 (C)	Quartz low, syn
01-087-0700 (C)	Diopside, syn
01-089-5402 (C)	Muscovite 2M1

Fig. 1: D4 ENDEAVOR diffractometer (right) and S4 PIONEER spectrometer (left) connected with conveyer belt. The D4 ENDEAVOR is equipped with Super Speed LYNXEYE^{TM} detector.

2) Combined XRD-XRF analysis

To confirm the phase identification results, and to obtain semi-quantitative phase amount estimates consistent with the actual elemental composition of the sample, combined XRD-XRF analysis has been performed with EVA. EVA enables semi-quantitative analysis based on the reference-intensity-ratio (RIR) method using both XRD as well as XRF data simultaneously: On scaling the maximum intensities of the ICDD PDF patterns to the observed peaks in the powder pattern, EVA calculates both phase and element concentrations, and compares the latter with the actually measured element concentrations.

Element concentrations as obtained by XRF and used by EVA are provided in Tab. 2. Already at first glance, the XRF data fully confirm the absence of any significant acid-producing ore minerals due to the minor concentrations found for heavy elements and the absence of sulphur.

The most accurate quantitative results will be obtained from a TOPAS Rietveld refinement. The combined XRD-XRF results obtained are of high value for defining the refinement model.
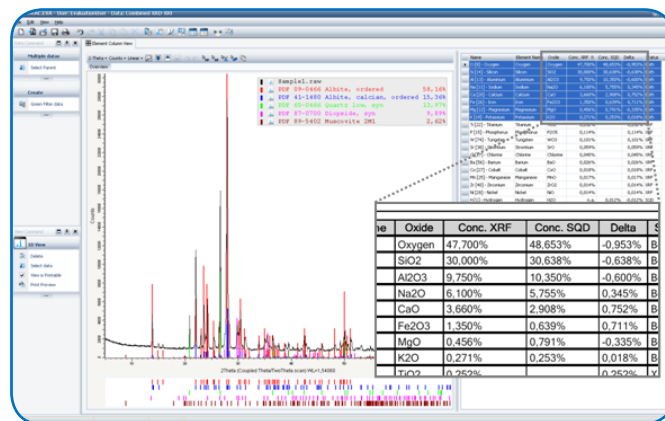

Fig. 3: EVA combined XRD-XRF results – comparison of calculated (column "SQD") versus observed (column "XRF") element concentrations. The difference is given in column "Delta".

Tab. 2: Element concentrations [%] as obtained by XRF.

Oxygen	47.7	Silicon	30.0
Aluminum	9.75	Sodium	6.1
Calcium	3.66	Magnesium	0.456
Iron	1.35	Potassium	0.271
Phosphorus	0.114	Chlorine	0.0445
Titanium	0.252	Manganese	0.0173
Cobalt	0.0182	Nickel	0.0142
Strontium	0.0595	Zirconium	0.0143
Barium	0.0258	Wolfram	0.101

Tab. 3: EVA semi-quantitative phase analysis results based on combined XRD-XRF using reference intensities as given in the ICDD PDF patterns.

SS-VVV-PPPP	Compound Name	Phase amounts
00-009-0466 (*)	Albite	58.2%
00-041-1480 (I)	Albite, calcian	15.4%
03-065-0466 (C)	Quartz low, syn	14.0%
01-087-0700 (C)	Diopside, syn	9.9%
01-089-5402 (C)	Muscovite 2M1	2.6%

The results for combined XRD-XRF analysis with EVA are shown in Fig. 3 and Tab. 3. The high Na vs. Ca concentrations confirm the presence of Na-plagioclase as found by XRD (diopside accounts for about 60% of the total Ca, as calculated by EVA). The present Na-plagioclase is most successfully modelled using two albite phases with different Ca amounts. Note the excellent agreement found between the calculated and observed element concentrations, which is better than 1% for all elements, and therefore confirms the correctness of the XRD phase identification results for all phases.

The accuracy of the RIR method is limited by several factors such as preferred orientation effects and the quality of the ICDD PDF data used (e.g. quality of relative intensities, I/Icor values, idealized chemical formula).

3) Quantitative TOPAS refinement

Quantitative Rietveld analysis has been performed using TOPAS, the results are shown in Fig. 4 and Tab. 4. For the final refinement two Na-plagioclases with different compositions have been used to model the data to take the elemental analysis results into account: Albite (0% Ca) and Oligoclase (25% Ca).

From the results in Tab. 4 the following conclusions can be drawn:

1. The sample can be unambiguously classified as a quartzdiorite according to Streckeisen, see Fig. 5.

2. Combined XRD-XRF analysis and TOPAS Rietveld refinement can allow a distinction of even neighboring plagioclase solid solution members (here albite and oligoclase) if present in sufficient amounts.

The present sample can be characterised as a rock with insignificant acid producing or neutralisation potential. Remarkable is the easy and reliable determination of the plagioclase type for estimation of the neutralisation potential. This ability is of particular interest, as anorthite has an about 14x higher neutralisation potential than albite (e.g. Jambor et al., 2002).
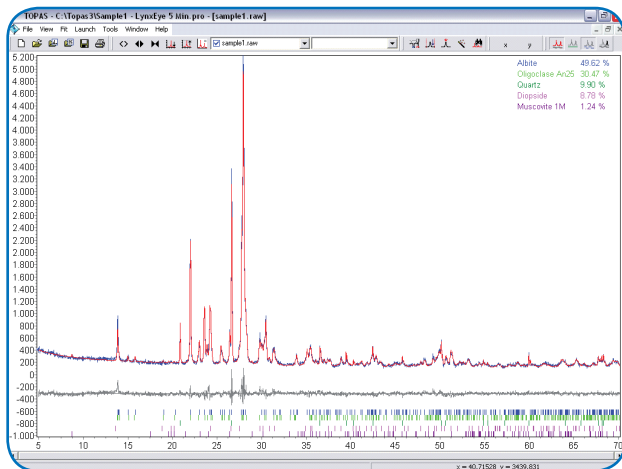

Fig. 4:   Quantitative TOPAS refinement results.

Tab. 4:   Quantitative TOPAS refinement results.

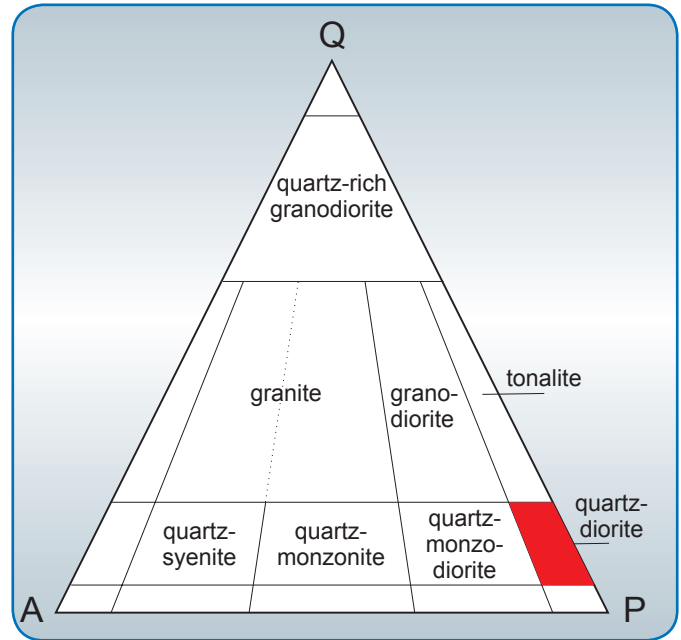| Compound Name	Phase amounts
Albite	49.6%
Oligoclase	30.5%
Quartz	9.9%
Diopside	8.8%
Muscovite	1.2%

Fig. 5:   Streckeisen diagram for intrusive rocks.
            Q: quartz, A: alkali-feldspar, P: plagioclase.

Reference

J.L. Jambor, J.E. Dutrizac, L.A. Groat, M. Raudsepp. Environmental Geology (2002) 43, 1–17.

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