

Normative calculation of mineral composition in Cr ores of the ophiolite complexes from SE Iran

Jamal Tarrah^{*}

Islamic Azad University, Bandar Abbas Branch, Geology Department, Bandar Abbas, Iran

Received 3 July 2015; accepted 11 December 2015

Abstract

Specific elements (Cr, Al, Ca, and Si) and loss on ignition (LOI) were used for semi-quantitative determination of the normative mineralogical composition of naturally occurring chromium ores in ophiolite complexes. By far the occurring ore minerals are complex both from the mineralogical and chemical viewpoints. The secondary minerals serpentine and Cr-containing chlorite (kaemmererite) form next to the spinel, the most abundant mineral in the ores. As a secondary formed mineral, Cr-containing garnet (uvarovite) is very rare. Among the primary minerals olivine occurs most often. Diopside plays a subordinate role. The amounts calculated for mineral associations of chromium ores occurring in south-eastern Iran are sufficiently accurate. The sum of calculated mineral contents varies from 83 to 108 wt. %. In the application of the normative procedure, Mg, Fe, Mn and Ni were not used for the calculation. Therefore, tests could be performed by comparing the measured Mg, Fe, Mn and Ni contents with the amounts of these elements deriving from normative calculation. The results are satisfactory, considering of the general problems of quantitative phase analysis of mineral associations.

Keywords: Normative calculation, Cr ores, Ophiolite complexes, SE Iran

1. Introduction

Variations in the chemical and mineralogical compositions of the naturally occurring chromium ores in ophiolite complexes help to understand not only the processes in the upper mantle and the magmatic evolution over time, but it also gives an indication of the post-magmatic events such as alterations during hydrothermalism. Thus, the occurrence of secondary silicate minerals reflects the intensity (P,T) and environmental characteristics (fluid exchange) of alteration. For example, serpentine usually forms under strong leaching conditions caused by abundant rainfall, good drainage, and acidic water from soil or sulphide oxidation. Therefore, for the study of ophiolite complexes and chromium ores contained in them as well as the characterization of the properties of climatic and environmental conditions in the geological past, the knowledge of quantitative mineralogical composition of both the original rock and the chromite ore is very important for petrologists. The quantitative mineralogical composition of geological samples is determined either directly by mineralogical analysis (modal) or the total chemical analysis (normative). The latter option requires knowledge of the qualitative mineralogical composition and chemical formulas of minerals.

*Corresponding author.

E-mail address (es): j.tarrah@yahoo.de

The limitations of the modal method have been extensively discussed in the literature (Flehmig 1983; Dultz and Reichenbach 1995; Dultz 1997; Fichter et al. 1998; Gehlken and Krakow 1998; Tarrah et al. 2000). However, if a direct quantitative analysis by X-ray diffraction combined with Rietveld analysis of mineral phases is not possible and chemical composition of occurring minerals can be known by microprobe analysis, then a calculation of the mineralogical composition with a normative method is an interesting option.

The aim of this study is to examine whether a normative calculation can successfully estimate the quantitative mineralogical composition of different chromium ores from south-eastern Iran. For this, a simple calculation method was used for the determination of the mineral contents. The origin for the normative method goes back to the CIPW norm (Cross, Iddings, Pirsson and Washington), which was a means of converting the chemical composition of the magmatic rocks to an ideal mineralogical composition (Cross et al. 1902). Originally only for the classification of igneous rocks based on their chemical analysis (Okrusch and Matthes 2013), the CIPW norm is being developed over more than a century with increasingly diverse modifications for different applications. Two recent works for the calculation of the mineralogical composition of the aggregates in the adhesive of the tile mortar (Ozkahraman and Işık 2005) and the use of the CIPW standard in assessing the specific measurements of rocks on Mars (McSween et al. 2008) must be mentioned.

In the present work, the CIPW standard has been modified. The basis of the calculation was XRF data from the powdered bulk rock and the oxide proportions (in percent) from the chemical composition of the specific minerals present in the samples identified with a microprobe. As a control of the normative method, the measured Mg, Fe, Mn and Ni contents by the XRF can be compared with the amounts of the same elements that resulted from the mineral contents derived from the normative calculation. This is based on the fact that the foregoing elements are not used in the calculation.

2. Geological area

Iran is composed of tectonic continental plates and micro plates of the Caledonian age (520-600 Ma). The continental terrenes are stitched together along sutures covered by Paleozoic and Mesozoic ophiolites. Mesozoic ophiolites of Iran are mostly belong to the Cretaceous are and are related to the Neo-Tethys ocean of the Mesozoic period. Most Mesozoic ophiolites of Iran show geochemical signatures that speak for suprasubduction zone (SSZ), which indicates that South West Asia was a place of plate convergence in the late Mesozoic time (Moghadam and Stern 2014).

The main chromite resources of Iran are found in ophiolites. For this work, the most frequently studied ores (except samples 3 and 6) are from the ophiolite complexes in the Makran zone, SE Iran (Fig. 1) and geographically situated in provinces Hormozgan and Sistan/Baluchistan. The Iranian Makran accretionary prism is a formation above the north-dipping subduction zone of the subduction of the Indian Oceanic crust (Siddiqui et al. 2012). The Makran accretionary prism geographically lies to the south of the Jaz Murian depression, extending for 450 km, from SE Iran to SW Pakistan. The Iranian Makran is a region about 200 km wide in SE Iran between the Jaz Murian depression and the Gulf of Oman.

Stoeklin (1984) classified the Alpine-Himalayan orogenic belt in Iran, Pakistan, Afghanistan, and Central Asia, into four groups: northern, southern, central and the axial ophiolite-bearing mountains. In relation to Iran, he discussed the internal and external ophiolite belts. As per this approach, the ophiolite complex of Esfandagheh with two samples, 3 and 6, (ES: in Figure 1) is probably from the internal belt. For host rock composition of the above-mentioned Samples 3 and 6 as well as the Sample No. 1/2/4/7 is no investigation is available. For the remaining samples-5/8/9/10-from the largest Iranian Cr deposit Faryab of the ophiolite complex Band-Zeyarat (Fig. 1) originate, in studies on platinum group elements petrology and composition of host rock was described in detail (Rajabzadeh and Moosavinasab 2013). According to their investigations, the ophiolite complex is divided into the two major parts: a) the north-western part including massive dunite, chromitite and harzburgite rocks with very minor contents of olivine clinopyroxene and wehrlite, and b) the south-eastern part that comprises nearly homogeneous foliated diopside harzburgite with minor amounts of dunite and lherzolite with few chromitites. Samples 5/8/9/10 come from the north-west part, containing high amounts of chromite. If harzburgite is present as an important rock in ophiolites, it is assumed that a basaltic magma had formed by the partial melting of the upper mantle and the remaining rock in the upper mantle had a composition of harzburgite.



Fig 1. Distribution map of ophiolithe complexes in Iran after Moghadam and Stern (2011) (with sampling points number 1–10 and Roads of Bandar Abbas to the locations for the sampling of Cr-ores)

Some researchers explain that the formation of basaltic magma was from the upper mantle lherzolite with the result that the remaining stones had the harzburgite composition. As that may be a possibility, the host rock was not investigated is in this work with paper being mainly concerned with the Cr ore from three ophiolite complexes Esfandagheh-Dolatabad, Chehelkureh (Nosratabad), and Band-Zeyarat (Fig.1).

3. Materials and methods

3.1. Cr-Ores and previous analyses

The normative calculation of mineral contents was applied to 10 Cr-ore samples of three ophiolite complexes from SE Iran. The location of these sites and a short macroscopic description of the collected ore samples are shown in Figure 1 and Table 1. These ore samples had been earlier analysed for chemical and mineralogical composition before (Tarrah and Abedpour 2014; Tarrah et al. 2015). All studies were performed at the Institute of Mineralogy-Geochemistry and Salt Deposits (Department of Repository Research of the Technical University of Clausthal, Germany).

For the presented normative calculation, the selected chemical data for Cr, Al, Ca, and Si and the LOI values from minerals and rock samples were taken from a previous work (Table. 2).

For the normative calculation, the contents of Cr, Al, Ca, and Si were taken, while the contents of Mg, Fe, Mn and Ni were used for the validation of the method of calculation. The chemical composition of bulk rocks was determined using X-ray fluorescence analysis. An X-ray diffractometer of the PAN analytical X pert pro type with copper tube was used as a device. The LOI values were not directly measured but calculated from the difference of 100 - Σ oxide contents. Usually, of the LOI is measured by heating samples at 1050°C and weighing. However, this could not be done in this study. The heating of Fe²⁺ containing samples can result in the oxidation of Fe³⁺.

Table 1: Sample name and sample numbers of Cr-ores determined with location and macroscopic description (Data from Tarrah et al. 2015)

| Sample name | Sample no. | Location | Macroscopic Description |
|-------------|------------|-----------------------|--------------------------------|
| Z.N.G | 1 | Nosratabad | massive Cr-ore with olivine |
| NJ | 2 | Manujan | massive Cr-ore |
| RX | 3 | Esfandagheh-Dolatabad | Cr-ore with banded olivine |
| MJ | 4 | Manujan | massive Cr-ore with serpentine |
| FB | 5 | Faryab mine | nodular Cr-ore |
| SF | 6 | Esfandagheh-Dolatabad | massive Cr-ore |
| RB | 7 | Barantin-Rudan | massive Cr-ore with chlorite |
| FAR 3 | 8 | Faryab mine | Pretreated Cr-ore |
| FAR 1 | 9 | Faryab mine | Cr-ore with green coating |
| FAR 2 | 10 | Faryab mine | Powder of Cr-ore |

Table 2: Selective chemical analysis by XRF and LOI values in wt. % (The data taken from Tarrah et al. 2015)

| Sample | ZNG | NJ | RX | MJ | FB | SF | RB | FAR3 | Far 1 | FAR2 |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Samp. no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Al ₂ O ₃ | 10.72 | 19.12 | 8.80 | 6.84 | 6.56 | 7.16 | 9.44 | 8.52 | 12.40 | 7.12 |
| MgO | 18.08 | 15.08 | 17.84 | 26.12 | 23.56 | 23.20 | 20.76 | 16 | 15.16 | 19.88 |
| CaO | - | 0.96 | 2.88 | 0.20 | 0.88 | 0.04 | - | 0.16 | 0.08 | 0.20 |
| MnO | 0.13 | 0.14 | 0.17 | 0.14 | 0.16 | 0.12 | 0.09 | 0.14 | 0.14 | 0.12 |
| NiO | 0.22 | 0.19 | 0.14 | 0.25 | 0.53 | 0.20 | 0.23 | 0.14 | 0.15 | 0.15 |
| ∑Fe as Fe₂O₃ | 15.68 | 14.68 | 15.28 | 11.04 | 14.88 | 12.72 | 12.48 | 15.20 | 16.32 | 13.48 |
| SiO ₂ | 18.10 | 4.28 | 19.95 | 24.67 | 20.09 | 18.42 | 8.99 | 6.82 | 8.13 | 13.49 |
| Cr ₂ O ₃ | 31.57 | 42.92 | 29.68 | 26.88 | 30.08 | 34.24 | 45.04 | 49.83 | 43.55 | 41.43 |
| LOI | 5.18 | 2.30 | 4.91 | 5.69 | 2.90 | 3.67 | 2.78 | 2.95 | 3.78 | 3.89 |

In the presence of high amounts of Fe^{2+} oxidation can lead to negative LOI values due to binding of additional O (Mirnejad and Lankarani 2014). As organic compounds in the ores are almost missing but in presence of small amounts of adsorbed water (H₂O⁻) due to the absence of fine-sized clay minerals, the LOI value is assumed to be structurally bound water (H₂O⁺).

According to the approach of previous works (Tarrah and Abedpour 2014; Tarrah et al. 2015), minerals were identified by X-ray diffractometry on non-oriented powder samples. The results were finally compared with those obtained by means of microprobe. All the samples contained a major phase spinel with silicate minerals occurring mainly in serpentine, chlorite, and sometimes olivine only locally. Diopside and uvarovite are minor constituents.

For the microprobe method (EMPA: Electron Micro Probe Analyses), polished sections of the ores were carefully studied using EDX for qualitative assessment and WDX for quantitative analysis. A four-channel CAMECA SX 100 electron microprobe was used as a device. The chemical homogeneity of the chromite grains and the associated silicates were confirmed by several microprobe traverses. The K α line was taken as the basis for the measurement of all elements. Table 3 shows the data for the mineral chemistry of the silicate phases and of the spinel for each sample (mean values of a different number of measurement points: n).

Table 3: Microprobe data for the chemistry of silicate minerals and of spinel phases in wt. % (n: number of measurement points, data from Tarrah and Abedpour, 2014)

| Sample Name | Sample Number | Olivine | | | | | | | | | | |
|----------------|------------------|---------|-------|--------------------------------|------------------|--------------------------------|----------|------|------------------|------|------|-------|
| | | n | MgO | Al ₂ O ₃ | SiO ₂ | Cr ₂ O ₃ | FeO | CaO | TiO ₂ | MnO | NiO | Total |
| ZNG | 1 | 5 | 52.3 | 0.01 | 42.7 | 0.01 | 4.4 | 0 | 0 | 0.05 | 0.7 | 100 |
| RX | 3 | 12 | 53 | 0 | 40.2 | 0.01 | 5.8 | 0 | 0 | 0.08 | 0.4 | 99.7 |
| FB | 5 | 12 | 54.1 | 0 | 42 | 0.01 | 4.1 | 0 | 0 | 0.07 | 0.6 | 101 |
| Far2 | 10 | 8 | 50.7 | 0.01 | 39.4 | 0.01 | 9.1 | 0.1 | 0 | 0.1 | 0.3 | 99.8 |
| Av | erage | | 52.5 | 0.005 | 41.1 | 0.01 | 5.9 | 0.02 | 0 | 0.07 | 0.5 | 100.1 |
| | | | | | | Py | roxene | | | | | |
| MJ | 4 | 4 | 18.3 | 0.9 | 52.7 | 1.09 | 1.1 | 25 | 0.1 | 0.03 | 0.1 | 99.2 |
| FB | 5 | 14 | 18.6 | 0.7 | 55.4 | 0.5 | 0.9 | 24 | 0 | 0.04 | 0.1 | 100 |
| Av | erage | | 18.4 | 0.8 | 54.05 | 0.7 | 1 | 24.5 | 0.05 | 0.03 | 0.1 | 99.6 |
| | | | | | | Sei | rpentine | | | | | |
| ZNG | 1 | 7 | 41.2 | 0.8 | 39.6 | 0.07 | 1.8 | 0 | 0 | 0.02 | 0.5 | 84.2 |
| RX | 3 | 12 | 42.2 | 0 | 42.7 | 0.008 | 3.4 | 0 | 0 | 0.05 | 0.2 | 88.7 |
| MJ | 4 | 6 | 40.3 | 0.2 | 34.3 | 0.5 | 5.1 | 0 | 0 | 0.05 | 0.8 | 81.4 |
| SF | 6 | 4 | 45.1 | 0.3 | 39.8 | 0.3 | 0.6 | 0 | 0 | 0.01 | 0.2 | 87.4 |
| Far3 | 8 | 3 | 41.1 | 0.8 | 42.2 | 0.3 | 1.4 | 0 | 0 | 0.01 | 0.1 | 86.1 |
| Far2 | 10 | 15 | 41.5 | 0.2 | 42.4 | 0.2 | 2.8 | 0 | 0 | 0.04 | 0.1 | 87.3 |
| Av | | 41.9 | 0.3 | 40.1 | 0.2 | 2.5 | 0 | 0 | 0.03 | 0.3 | 85.8 | |
| | | | | | | Cł | nlorite | | | | | |
| NJ | 2 | 7 | 34.1 | 13.8 | 32.7 | 5.1 | 3.4 | 0.1 | 0.1 | 0.02 | 0.3 | 89.6 |
| FB | 5 | 2 | 31.6 | 18.3 | 31.4 | 1.6 | 0.9 | 0.8 | 0.2 | 0.04 | 0.4 | 87.4 |
| SF | 6 | 10 | 36.1 | 14.9 | 33.4 | 3.3 | 1.1 | 0 | 0 | 0.01 | 0.3 | 89.3 |
| RB | 7 | 8 | 36.1 | 15 | 32.4 | 2.7 | 0.4 | 0 | 0 | 0.01 | 0.3 | 87.1 |
| Far3 | 8 | 9 | 36.6 | 13.7 | 34.2 | 2.8 | 1.1 | 0 | 0 | 0.01 | 0.2 | 88.8 |
| Farl | 9 | 11 | 36.3 | 15.4 | 33.3 | 3.1 | 0.9 | 0 | 0 | 0.01 | 0.2 | 89.3 |
| Av | erage | | 35.1 | 15.1 | 32.9 | 3.1 | 1.3 | 0.1 | 0.05 | 0.01 | 0.2 | 88.5 |
| | | 0 | 0.2 | 4.2 | 25.2 | Uv | arovite | 25 | 2.0 | 0.02 | | 00.6 |
| NJ | 2 | 8 | 0.3 | 4.3 | 35.2 | 17.5 | 2.3 | 35 | 3.9 | 0.02 | 0 | 98.6 |
| Farl | 9 | 14 | 0.09 | 3.4 | 36.8 | 23.2 | 1.8 | 34 | 0.4 | 0.01 | 0 | 100 |
| Av | erage | | 0.2 | 3.8 | 36 | 20.3 | 2.05 | 34.5 | 2.1 | 0.01 | 0 | 99.3 |
| 700 | | 20 | 14.94 | 12.29 | | 54 49 | 16.82 | | 0.25 | 0.17 | 0.15 | |
| ZNG | 1 | 28 | 14.84 | 12.38 | - | 54.48 | 10.82 | - | 0.25 | 0.17 | 0.15 | |
| NJ | 2 | 30 | 15.09 | 20.80 | - | 49.37 | 13.47 | - | 0.18 | 0.14 | 0.15 | |
| RX | 3 | 19 | 12.45 | 11.71 | - | 55.22 | 19.04 | - | 0.28 | 0.23 | 0.07 | |
| MJ | 4 | 40 | 13.72 | 13.46 | - | 56.49 | 16.21 | - | 0.19 | 0.19 | 0.08 | |
| FB | 5 | 22 | 12.31 | 10.96 | - | 55.62 | 19.33 | - | 0.20 | 0.22 | 0.07 | |
| SF | 6 | 27 | 14.22 | 6.46 | - | 60.69 | 17.73 | - | 0.14 | 0.21 | 0.07 | |
| RB | 7 | 21 | 16.34 | 10.32 | - | 58.17 | 13.27 | - | 0.13 | 0.14 | 0.16 | |
| Far3 | 8 | 18 | 13.37 | 8.81 | - | 61.25 | 16.54 | - | 0.14 | 0.18 | 0.09 | |
| Far1 | 9 | 26 | 12.85 | 10.95 | - | 58.99 | 16.45 | - | 0.15 | 0.17 | 0.09 | |
| Far2 | 10 | 16 | 14.00 | 10.28 | - | 59.91 | 15.95 | - | 0.13 | 0.17 | 0.08 | |

3.2 Method of normative calculation

The elements Cr, Al, Ca, Si and LOI were selected for normative calculation based on the identified minerals by modal analyses using XRD. The average values of these elements, with the exception of Cr, determined from the microprobe for the calculation process, are given in bold in Table 3. For the calculation of the spinel, no average was calculated. Values for LOI, as discussed already in 3.1, result from the difference between the average 'Total' and 100%. The mineralogical composition of the bulk samples was calculated as follows.

Elements that are components of only one of the considered minerals were fully assigned to these minerals. This was only the case for Cr, but here the limitation was that chlorite present in the ores contained, on average, about 3.1 wt. % Cr₂O₃ (Table. 3). This issue was taken into account in the calculation (see Step 3). The contents of the elements that occur in more than one mineral were successively reduced from the total amount until they were fully allocated in the relevant minerals. The calculation is based on findings by modal analysis. If a mineral phase did not occur in the modal analysis, it was not included in the calculation. The calculation sequence is briefly explained in seven consecutive steps:

1. In the first step, the content of spinel in the ore is calculated by the equation $[Cr_2O_3\ _{(XRF)}X\ 100\ /\ Cr_2O_3\ _{(EMPA)}]$. The difference from 100 then yields the sum of associated silicates or gangue minerals.

2. Al_2O_3 (XRF), reduced of its content of spinel calculated in Step 1, is assigned to chlorite, with an average Al_2O_3 of 15.1 wt. % (Table. 3) for chlorite.

3. Owing to the presence of an average of 3.1 wt. % Cr_2O_3 in chlorite, the calculation of the spinel in this step is repeated. This time, the total Cr_2O_3 (XRF) is reduced by its share in chlorite and the remaining Cr_2O_3 used to calculate spinel.

4. In this step, the LOI(XRF) value, reduced of its share in

chlorite, is used for the calculation of serpentine, with an average LOI of 14.2 wt. % for this mineral (Table. 3: 100 - 85.8 = 14.2).

5. From the value for CaO $_{(XRF)}$, the amount of diopside is calculated, with an average of 24.5 wt.% CaO for diopside (Table. 3).

6 . Then, with the residual $SiO_{2 (XRF)}$, where the shares in chlorite, serpentine and pyroxene were subtracted from total content, olivine is calculated, with an average of 41.2 wt. % SiO_2 (Table. 3).

7. The difference of $100 - \Sigma$ (spinel + chlorite + serpentine + diopside + olivine) then results in the value for uvarovite. This is possible because uvarovite occurs in small amounts, as revealed by analysis, in the samples that do not contain olivine and pyroxene. Therefore, Si and Ca values do not need to be corrected.

4. Results and discussion

4.1. Normative mineralogical composition

On the basis of examination with XRD and microprobe, the bulk of the mineralogical composition of chrome ores is composed, in addition to spinel, of the gangue minerals serpentine, chlorite, olivine, diopside and uvarovite in varying mineral association of the foregoing compounds and in varying proportions. The typical ore generally contains, with exception of Samples 5 and 7, two silicate minerals. The ores are mineralogically divided into the following six groups (Tarrah and Abedpour 2014; Tarrah et al. 2015):

Cr-rich spinel, olivine and serpentine group (Samples 1, 3, 10)

Cr-rich spinel, diopside and serpentine group (Sample 4)

Cr-rich spinel, diopside, olivine and chlorite group (Sample 5)

Cr-rich spinel, chlorite and serpentine group (Samples 6, 8) Cr-rich spinel, chlorite group and uvarovite (Samples 2, 9)

Cr-rich spinel and chlorite group (Sample 7)

The results of the calculation for the mineral phases of the above six groups are shown in Table 4.

| Sample | Sample | a | g = 100 - a | b | c | d | e | f | $\sum(a+b+c+d)$ |
|--------|--------|--------|-------------|----------|------------|----------|---------|-----------|-----------------|
| name | no. | Spinel | ∑ Gangue | Chlorite | Serpentine | Diopside | Olivine | Uvarovite | +e+f) |
| | | | minerals | | | | | | |
| ZNG | 1 | 58.0 | 42.0 | _ | 36.5 | _ | 8.8 | _ | 103.3 |
| NJ | 2 | 86.5 | 13.5 | 7.4 | _ | _ | _ | 6.1 | 100.0 |
| RX | 3 | 53.8 | 46.2 | _ | 34.5 | _ | 12.7 | _ | 101.0 |
| MJ | 4 | 47.6 | 52.4 | _ | 35.6 | 0.8 | _ | _ | 83.2 |
| FB | 5 | 53.6 | 46.4 | 4.4 | _ | 3.6 | 40.7 | _ | 102.3 |
| SF | 6 | 55.2 | 44.8 | 23.8 | 8.0 | _ | _ | _ | 87.0 |
| RB | 7 | 76.9 | 23.1 | 10.0 | _ | _ | _ | _ | 86.9 |
| Far3 | 8 | 80.9 | 19.1 | 9.2 | 13.5 | _ | _ | _ | 103.6 |
| Far1 | 9 | 72.3 | 27.7 | 29.7 | _ | _ | _ | _ | 102.0 |
| Far2 | 10 | 69.0 | 31.0 | _ | 27.3 | _ | 11.4 | _ | 107.7 |

Table 4: Normative mineralogical composition of the ores in wt. %.

Calculations showed the lowest content of spinel (47.6 wt. %) in Sample 4 and the highest amount (86.5 wt. %) in Sample 2. The difference of the value of spinel from 100 wt. % showed the sum of the gangue minerals (Table 4, indicated in column 'g'). The chlorite varied more strongly. Its proportion was between 4.4 wt. % (Sample 5) and 29.7 wt. % (Sample 9). This was also true of serpentine with the values of 8.0 wt. % (Sample 6) and 36.5 wt. % (Sample 1). Diopside only occurred with 0.8 wt. % in Sample 4 and with 3.6 wt. % in Sample 5. The content of olivine was between 8.8 wt. %

(Sample 1) and 40.7 wt. % (Sample 5). From Table 3 shows that all samples except Sample 4 contained more than 50% spinel. Hence, the site, Manujan, had not been considered in the past for mining (Tarrah et al. 2015). All minerals of the six groups were found by the

All minerals of the six groups were found by the normative calculation, apart from uvarovite in Sample 9 (Table 4). In addition, uvarovite was marginally present in Sample 2, which is due to the low CaO content derived from chemical analysis of bulk sample by XRF. In Sample 9, the element Ca is considered only a part of the uvarovite (Table 3). From microprobe data, the structural formula of uvarovite was calculated on the basis of 12 oxygen and the differentiation of divalent and trivalent iron: $[Ca_{3.05} Fe(II)_{0.03} Mg_{0.03}]$ [Cr_{1.32} Fe(III) _{0.11} Al_{0.37} Ti_{0.13}] Si_{2.97} O₁₂. As can be seen from Table 2, CaO in Sample 9 is 0.08 wt. % only. Sample 2 contains about 0.2 wt. % uvarovite, considering the 34.5% CaO content in uvarovite (Table 3).

Considering the problems of the quantitative phase analysis, the results obtained by normative calculation are overall satisfactory. The total amounts of calculated minerals varies approximately between 83 (Sample 4) and 108 wt. % (Sample 9). However, since the sum of mineral contents of three samples (4/6/7) lies between 83 until 87%, it is concluded, that these ores are not completely described by modal analysis with respect to their mineralogical composition. In the next section, a validation is performed with Mg and Fe as the main elements as well as Mn and Ni as trace elements in the ores. These four elements were not included in earlier calculations.

4.2. Validation of the method using contents of Mg, Fe, Mn and Ni

In the normative method used, Mg, Fe, Mn and Ni were not included in the calculation. Therefore, the validity of the method was tested by comparing the measured Mg, Fe, Mn and Ni contents with the contents calculated by the normative method (Fig. 2a-d). Data of the Mg, Fe, Mn and Ni contents bound in minerals can be derived for each sample from the chemistry of minerals obtained by microprobe analysis (Table. 3). The validity of the normative calculation is indicated by one-to-one relations (1:1 lines in Fig. 2).

The difference between the normatively (n) calculated and chemically (c) analysed contents [(n-c) c⁻¹ X 100] is for Mg 17% (mean value) \pm 29% (standard deviation). For Fe, Mn and Ni contents are there: $-9\% \pm 8\%$ (Fe), $-4\% \pm 13\%$ (Mn) and $-13\% \pm 33\%$ (Ni). The application of the method gave on average for 10 samples higher normative Mg contents and lower Fe, Mn and Ni contents than expected by the total chemical analysis (Fig. 2). In comparison, Mg shows a maximum deviation followed by Ni, Fe and Mn (Fig. 2).

Generally speaking, no plausible explanation is possible for the 10 samples with the overestimation and uncertainties of MgO (calc.). Here the approach is more promising for taking specific samples into consideration. For Sample 7, there is a considerable underestimation of MgO (calc.). A MgO phase is visible in the corresponding BSE image (Fig. 3), which is probably due to its low content that was not detectable with X-ray and the microprobe. Whether the existence of this MgO phase in absolute terms might explain a higher content of about 4.5 wt. % MgO analysed, cannot be proved with the existing data.

The underestimation for Fe and Ni may partly be due to the fact that in the ores other subordinated Fe and Nicontaining mineral phases occur such as Ni sulphides or oxides of Fe. These phases are co-analysed chemically. Moreover, they are recognizable in the BSE image (Fig. 4).

The image is that of Sample 5, in which the measured value of Ni shows an excess of about 40% against the calculated value. From Figure 4, the existence of several Fe and Ni phases such as NiO, NiS, NiFeS, and Fe-oxides could be deduced. Even a Ni, Mg, and Si a connection in one mineral is evident. Owing to their low contents and probably also due to the poor crystallinity of these probably secondary phases, they are not detectable by X-ray diffraction. In the normative procedure the minerals, which were clearly present in the X-ray diffraction pattern, were calculated. The same explanation may therefore apply to Mn that has the lowest difference in the validation. It is well-known that the Mn can replace Fe in the crystal lattice.

4.3. Limits of validation using Al and Si

Restrictions exist for the validation of normative calculation using with the common elements Al and Si, which are present in many silicates. Al has been assigned to the chlorite and Si to the olivine. In samples without presence of chlorite Al was compared from the normative calculation with the Al from the XRF analysis. Similarly, it was also made for Si in samples without olivine (Table. 5). While the calculated values from the normative calculation in comparison with the measured values show no great variation in Al₂O₃ with - 17% ±16 (mean value ±16 standard deviation), on the other hand, the relative difference in SiO₂ is clearly larger (-24% ±35). The slightest deviation in SiO₂ for Sample 2 recorded to be 7% and Al₂O₃ for Sample 10 to be 0% (Table. 5).



Figure 2: MgO (a), FeO (b), MnO (c) and NiO (d) contents of ore samples calculated with the normative method (MgO_{calc.}, FeO_{calc.}, MnO_{calc.} and NiO_{calc.}) vs. chemically analysed MgO, FeO, MnO and NiO contents (MgO_{anal.}, FeO_{anal.}, MnO_{anal.} and NiO_{anal.})



Fig 3. BSE image of Sample No. 7 from Barantin-Rudan, combined with the mineral chlorite

Fig 4. BSE image of Sample No. 5 from Faryab mine

| Sample name | Sample no. | anal. SiO ₂ (c) | calc. SiO ₂ (n) | [(n – c) c ⁻¹ X 100] | Sample name | Sample no. | anal. Al ₂ O ₃ (c) | calc. Al ₂ O ₃ (n) | [(n – c) c ⁻¹ X 100] |
|----------------|---------------|-------------------------------|-------------------------------|------------------------------------|----------------|---------------|---|---|------------------------------------|
| NJ | 2 | 4.28 | 4.57 | 7 | ZNG | 1 | 10.72 | 7.18 | -33 |
| MJ | 4 | 24.67 | 12.54 | -49 | RX | 3 | 8.8 | 6.3 | -28 |
| SF | 6 | 18.42 | 11.13 | -40 | MJ | 4 | 6.84 | 6.41 | -6 |
| RB | 7 | 8.99 | 3.34 | -63 | Far 2 | 10 | 7.12 | 7.09 | - |
| Far 3 | 8 | 6.82 | 8.86 | 30 | Mean | | | | -17 |
| Far 1 | 9 | 13.49 | 9.89 | -27 | St Dev. | | | | ±16 |
| Mean | | | | -24 | | | | | |
| St Dev. | | | | ±35 | | | | | |

Table 5: Comparison between SiO₂ and Al₂O₃ contents in wt. % calculated with the normative (n) method and chemically (c) analysed values (SiO₂ in the case of samples without olivine and Al₂O₃ in samples without chlorite)

Especially large is the variation in Sample 7 with a normative value of 3.34 wt. % SiO₂, compared to the measured value of 8.99 wt. %. The discrepancy cannot be explained straightaway. However, it could probably be due to the presence of an amorphous Si phase, but this could not be detected by XRD. Here, an alkaline extraction would be most promising for identification. According to Table 4, the sum of calculated minerals in Sample 7 is 86.9 wt. %. Here, it has to be considered that this is the sample with the MgO phase detectable by microprobe. Whether the difference to 100% can be explained with a MgO and a discrete Si phase remains open.

5. Concluding remarks

The problem of quantitative determination of mineral phases in rocks cannot be circumvented merely by chemical analysis and with calculated normative mineral contents, if the chemistry of common minerals in the samples such as chlorite and serpentine show great variation. The investigation on different Cr ores reveals that only precise qualitative modal analysis and the simultaneous determination of the chemical composition of the bulk rock samples together with the mineral chemistry of the occurring phases provide the prerequisite for a meaningful normative calculation. This way, information on supply and removal of chemical elements, correlation and interpretation of element concentrations as well as the alteration of the mineralogical composition can be obtained. Based on the modal analyses and the normative calculation of mineralogical composition of 10 samples from ophiolite complexes in SE Iran, it can be concluded that mineral alteration in Cr ores caused the formation of different silicate minerals in varying mineral association and in varying proportions, strongly depending on the nature of the ore and the strength and mode of the alteration. Here, changes by processes of serpentinization and chloritization were clearly identified. Despite some considerable deviation between the chemical analyses and normative data of elements from the calculated minerals, the normative method proved to be useful to quantitatively estimate

the mineralogical composition of Cr ores in different ophiolite complexes.

Acknowledgements

The author is grateful to the Islamic Azad University of Bandar Abbas (Iran) and the Technical University of Clausthal (Germany) for the approval of this research programme and the financial support. My special thanks go to the head of the Institute of Mineralogy-Geochemistry and salt deposits (Department of Repository Research of the Technical University of Clausthal, Germany) Prof. Dr. K. Mengel and his staff for suggestions, critical discussion, and help in the preparation of samples for analyses.

References

- Cross W, Iddings JP, Pirsson LV, Washington HS (1902) A quantitative chemico-mineralogical classification and nomenclature of igneous rocks, *The Journal of Geology* 10:555-690.
- Dultz S (1997) Textur der mineralischen Substanz, in H.-P.Blume, P. Felix-Henningsen, W. R. Fischer, H.-G. Frede, R. Horn and K. Stahr (Eds.): Handbuch der Bodenkunde 1, Landsberg: 1-16.
- Dultz S, Reichenbach HGV (1995) Quantitative Mineralbestimmung in der Schlufffraktion von Böden auf der Grundlage der chemischen Analyse und unter Anwendung der Karl-Fischer-Titration. I. Verfahren, Zeitschrift für Pflanzenernährung und Bodenkunde 158:453-458.
- Fichter J, Bonnaud P, Turpault MP, Ranger J (1998) Quantitative determination of minerals in acid forest soils of granite, *Zeitschrift für Pflanzenernährung und Bodenkunde* 161:129-139.
- Flehmig W (1983) Mineral composition of pelitic sediments in the Rhenohercynian Zone. In: Intracontinental fold belts. Springer, pp 257-265.
- Gehlken P-L, Krakow L (1998) Quantitative infrarotspektroskopische Bestimmung von Quarz bzw. freier Kieselsäure in keramischen Rohstoffen, *Keramische Zeitschrift* 50:91-93.
- McSween HY, Ruff SW, Morris RV, Gellert R, Klingelhoefer G, Christensen PR, McCoy TJ, Ghosh

A, Moersch JM, Cohen BA (2008) Mineralogy of volcanic rocks in Gusev crater, Mars: Reconciling Mössbauer, Alpha Particle X-Ray Spectrometer, and Miniature Thermal Emission Spectrometer spectra, *Journal of Geophysical Research: Planets* 113.

- Mirnejad H, Lankarani M (2014) Analytical Techniques in Geoscience, University of Tehran press, 322 p. (in Persian).
- Moghadam HS, Stern RJ (2011) Late Cretaceous forearc ophiolites of Iran, *Island Arc* 20:1-4.
- Moghadam HS, Stern RJ (2014) Ophiolites of Iran: Keys to understanding the tectonic evolution of SW Asia:(I) Paleozoic ophiolites, *Journal of Asian Earth Sciences* 91:19-38.
- Okrusch M, Matthes S (2013) Mineralogie: eine Einführung in die spezielle Mineralogie, Petrologie und Lagerstättenkunde. Springer-Verlag.
- Ozkahraman H, Işık E (2005) The effect of chemical and mineralogical composition of aggregates on tensile adhesion strength of tiles, *Construction and Building Materials* 19:251-255.
- Rajabzadeh MA, Moosavinasab Z (2013) Mineralogy and distribution of Platinum-Group Minerals (PGM) and other solid inclusions in the Faryab ophiolitic

chromitites, Southern Iran, *Mineralogy and Petrology* 107:943-962.

- Siddiqui RH, Jan MQ, Khan MA (2012) Petrogenesis of late Cretaceous lava flows from a Ceno-Tethyan island arc: The Raskoh arc, Balochistan, Pakistan, *Journal of Asian Earth Sciences* 59:24-38.
- Stoeklin J (1984) The Tethys paradox in plate tectonics, *Plate Reconstruction from Paleozoic Paleomagnetism: Interim Report of Working Group 2 on Phanerozoic Plate Motions and Orogenesis* 12:27.
- Tarrah J, Abedpour Z (2014) The study of the chemical composition from silicate phases in chrome ores, SE of Iran.18th Symposium of the Geological Society of Iran, pp. 916-923. (in Persian).
- Tarrah J, Abedpour Z, Strauss K, Schirmer T, Mengel K (2015) Mineralogical and geochemical investigations of chromite ores from ophiolite complexes of SE Iran in terms of chrome spinel composition, *Iranian Journal of Earth Sciences* 7:114-123.
- Tarrah J, Meiwes KJ, Meesenburg H (2000) Normative calculation of minerals in North German Loess soils using the modified CIPW norm, *Journal of Plant Nutrition and Soil Science* 163:307-312.