

A Norm Calculation Method Using Square Matrix: Implications for the Total Volume Estimation of Microscale Ore Minerals

著者	NISHIMURA Koshi, WATANABE Yasusi, SANEMATSU Kenzo, HOSHINO Mihoko, TAKAGI Tetsuichi
著者別名	西村 光史, 渡辺 寧, 実松 健造, 星野 美保子, 高木 哲一
journal or publication title	Journal of Toyo University. Natural science
volume	57
page range	63-72
year	2013-03
URL	http://id.nii.ac.jp/1060/00005993/



A Norm Calculation Method Using Square Matrix: Implications for the Total Volume Estimation of Microscale Ore Minerals

Koshi NISHIMURA^{1,2}, Yasushi WATANABE², Kenzo SANEMATSU²,
Mihoko HOSHINO², Tetsuichi TAKAGI²

Abstract

An approach using square matrix is employed to calculate mineral volume abundance from whole-rock composition. Mineral species and those chemical compositions are treated as known parameters. The volume abundances of the minerals can be determined simultaneously from whole-rock element data without assignment of whole-rock FeO/Fe₂O₃ ratio. This approach has been tested for some holocrystalline rocks and a good agreement with point-counting results has been obtained. In principle, the present method can be applied to any type of rock. Ore minerals in ore are sometimes too small for point-counting analysis. In such a case, the present norm calculation method becomes a useful tool to estimate the mineral volume abundance.

Keywords: norm calculation, CIPW, iron-oxidation ratio, square matrix, ore mineral, modal analysis

1. Introduction

Total volume estimation of the ore mineral in the ore provides crucial information to evaluate mineral-resource potential. One of the most popular methods of mineral volume analysis is the point-counting under optical microscope. However, this method is not available for the rocks with cryptocrystalline minerals or with microscale minerals whose size is greatly less than the thickness of the thin section (~35 μm). Economic and sub-economic deposits often contain the microscale minerals that are enriched in useful elements such as REEs. In such cases, the volume of ore minerals can be briefly estimated using data of whole rock and mineral chemistry.

Numerous norm calculation methods have been used over a century to estimate abundances of standard minerals from the whole-rock chemical data of igneous rocks.

¹ Natural Science Laboratory, Toyo University, 5-28-20 Hakusan, Bunkyo-ku, Tokyo 112-8606, Japan

² Institute for Geo-Resources and Environment, Geological Survey of Japan, AIST No. 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

The idea of the norm calculation was first introduced into petrology by W. Cross, J. P. Iddings, L. V. Pirsson, and H. S. Washington (CIPW norm; Cross *et al.*, 1902) and there have been a number of modifications and refinements (e.g. Washington, 1917; Johannsen, 1931; Kelsey, 1965; Cox *et al.*, 1979; Ragland, 1989; Verma *et al.*, 2002). The norm calculation schemes using square matrix have also been developed (e.g. Nishimura & Yanagi 2000; Pruseth 2009). These calculation schemes need to assign whole rock FeO/Fe₂O₃ ratio. Unfortunately, however, there is no standardized method for apportionment the oxidation ratio to the rocks whose Fe₂O₃ and FeO contents were not separately determined (Verma *et al.*, 2002). The results of the conventional norm calculations vary greatly depending on the adjustment method of Fe-oxidation ratio (e.g. Le Maitre 1976; Middlemost 1989). In addition, most conventional models were not designed for the minerals those are rare in igneous rocks. We develop a simple norm calculation method that is applicable not only to igneous rocks but also to any other rocks without assignment of the oxidation ratio.

Advances in micro-analytical technique, such as EPMA and LA-ICP-MS, now allow the accurate chemical analysis for almost all rock-forming minerals even if a rock consists of microscale minerals. Our model treats mineral species and those chemical compositions as known parameters. In this case, mineral contents can be calculated from whole-rock element data using square matrix without assignment of whole-rock FeO/Fe₂O₃ ratio. Once the mineral compositions and proportions are fixed, the whole-rock iron-oxidation ratio is inevitably determined. This method can be applied to the ore minerals whose size is too small for point-counting analysis.

Table 1 Mineral parameters used in the calculation

Mineral	Formula	Molecular weight	Specific gravity*
Fluorite	CaF ₂	78.08	3.18
Hematite	Fe ₂ O ₃	159.70	5.25
Magnetite	FeO·Fe ₂ O ₃	231.55	5.2
Quartz	SiO ₂	60.09	2.65
Goethite	FeO·OH	88.86	4.3
Phlogopite	K ₂ Mg ₆ [Si ₆ Al ₂ O ₂₀](OH) ₄	834.59	3
Annite	K ₂ Fe ₆ [Si ₆ Al ₂ O ₂₀](OH) ₄	1023.83	3
Fluorapatite	Ca ₅ (PO ₄) ₃ F	504.31	3.23
Monazite-(Ce)	CePO ₄	235.07	5.15
Celestine	SrSO ₄	183.69	3.96

*Deer et al. (1992)

2. Method

Norm calculation begins with conversion of the analysis in weight percent to molecular form. The molecular proportion of each constituent is determined by dividing by the appropriate molecular weight. Conventional norm calculation methods recast the molecular proportion of each oxide into a series of normative minerals and simultaneously determine the normative mineral assemblages. However, most of the conventional methods were designed for igneous rocks and could not be directly applicable to the other types of rock such as hydrothermally mineralized rocks. The present norm calculation method permits the pre-selection of desired minerals of analyzed composition and treats those as known parameters. The chemical mass balance between a rock sample and its constituent minerals can be expressed as:

$$y_i = \sum_{j=1}^m a_j x_{ij} \quad (1)$$

where y_i is the molecular proportion of an element in the rock sample, a_j is the molecular proportion of a mineral, x_{ij} is the moles of an element per mole of a mineral formula, m is the number of mineral phases present in the rock sample. If we select the same number of elemental components as mineral phases, Eq. (1) can be expressed by using square matrix (Nishimura & Yanagi 2000; Pruseth 2009) as:

$$\begin{pmatrix} x_{11} & \cdots & x_{1j} & \cdots & x_{1m} \\ \vdots & & \vdots & & \vdots \\ x_{i1} & \cdots & x_{ij} & \cdots & x_{im} \\ \vdots & & \vdots & & \vdots \\ x_{m1} & \cdots & x_{mj} & \cdots & x_{mm} \end{pmatrix} \begin{pmatrix} a_1 \\ \vdots \\ a_j \\ \vdots \\ a_m \end{pmatrix} = \begin{pmatrix} y_1 \\ \vdots \\ y_j \\ \vdots \\ y_m \end{pmatrix} \quad (2)$$

Although conventional models have generally adopted oxides as whole rock component, there is no universally accepted method for the adjustment of iron-oxidation ratio as noted above. The present method use elements as whole rock component (y_i), instead of oxides. Equation (2) can also be expressed as:

$$\begin{pmatrix} a_1 \\ \vdots \\ a_j \\ \vdots \\ a_m \end{pmatrix} = \begin{pmatrix} x_{11} & \cdots & x_{1j} & \cdots & x_{1m} \\ \vdots & & \vdots & & \vdots \\ x_{i1} & \cdots & x_{ij} & \cdots & x_{im} \\ \vdots & & \vdots & & \vdots \\ x_{m1} & \cdots & x_{mj} & \cdots & x_{mm} \end{pmatrix}^{-1} \begin{pmatrix} y_1 \\ \vdots \\ y_j \\ \vdots \\ y_m \end{pmatrix} \quad (3)$$

The inverse matrix in the right-hand side can easily be calculated by using intrinsic functions of spreadsheet software such as MS-Excel. Once the inverse matrix is calculated, the molecular proportions of the all minerals can be determined simultaneously. The estimation error of the mineral proportion depends on the uncertainty in whole-rock and mineral analyses (Eq. 3). If the given whole-rock and mineral compositions are accurate, the estimation of the mineral proportion also becomes accurate. Once the mineral proportions are determined, whole-rock Fe-oxidation ratio can be calculated from the mineral compositions.

When two or more minerals differ only in oxidation state (e.g., magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) and hematite (Fe_2O_3) in Fig. 1a), we use the mean composition of those minerals. If the relative volume ratio between those minerals is obtained by using optical microscope or electron microprobe, the mean composition can be easily calculated as follows. For example, when the magnetite to hematite volume ratio is estimated as r , the following mass balance equation is formed:

$$\alpha = (rD^{\text{Mag}}Mw^{\text{Hem}}) / (D^{\text{Hem}}Mw^{\text{Mag}}) \quad (4)$$

where α is the molecular ratio of magnetite divided by the molecular ratio of hematite, D^{Mag} is the specific gravity of magnetite, D^{Hem} is the specific gravity of hematite, Mw^{Hem} is the molecular weight of hematite and Mw^{Mag} is the molecular weight of magnetite. By using Eq. (4), the mean formula of magnetite and hematite can be defined as $\alpha(\text{FeO}\cdot\text{Fe}_2\text{O}_3)\cdot\text{Fe}_2\text{O}_3$. Adopting the values of these parameters in Table 1, Eq. (4) can be rewritten as

$$\alpha = 0.68r \quad (5)$$

Molecular ratio of $\alpha(\text{FeO}\cdot\text{Fe}_2\text{O}_3)\cdot\text{Fe}_2\text{O}_3$ can be calculated by using square matrix in the same way as described above. Weight percent of hematite (or magnetite) is obtained by multiplying the molecular weight of Fe_2O_3 (or $\alpha(\text{FeO}\cdot\text{Fe}_2\text{O}_3)$) by the molecular ratio of $\alpha(\text{FeO}\cdot\text{Fe}_2\text{O}_3)\cdot\text{Fe}_2\text{O}_3$.

Table 2 Comparison between normative and modal abundance of minerals in fluorite-hematite ore (sample P02)

Mineral	Norm (wt %)	Norm* (vol %)	Mode (vol %)
Hematite	64.75 ± 1.26	56.65 ± 1.10	55.37 ± 1.97
Fluorite	30.01 ± 0.58	43.35 ± 0.84	44.63 ± 1.97

* Volume percentages are normalized to total 100 % for comparison with modal analysis

3. Application to natural rock

The effectiveness of the present norm calculation is verified by comparison between the normative and modal abundances of natural rocks. Here we show three examples of the application of the present model to mineralized rocks. The whole-rock chemical compositions were determined by a lithium metaborate/tetraborate fusion ICP-MS package at Activation Laboratory, Ancaster, Ontario in Canada. The mineral formulas were estimated based on EPMA (JEOL JXA-8900R) analyses at the Geological Survey of Japan. The modal analyses were conducted following the procedure reported by Neilson and Brockman (1977).

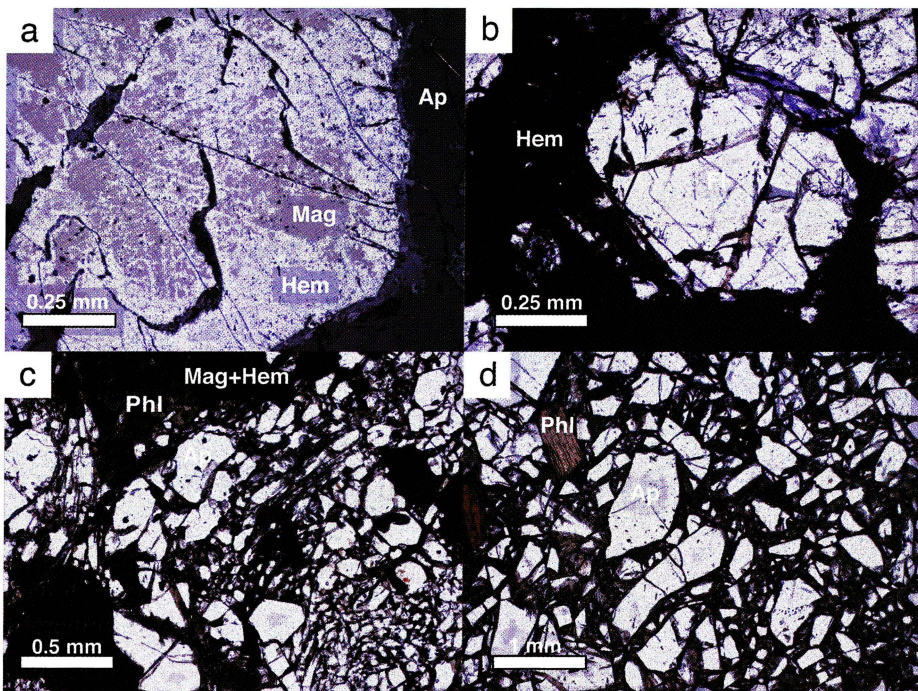


Figure 1 Photomicrographs of thin sections of ore samples under reflected (a) and transmitted (b–d) light. (a) Holocrystalline apatite ore (sample P700D) in the Mushgia Khudag hydrothermal deposits, Mongolia. The magnetite is partly oxidized to hematite. (b) Fluorite-Hematite ore (sample P02) related to the activity of the Bushveld granite, South Africa. (c) Holocrystalline texture of the apatite ore, sample P700D. (d) Porphyritic apatite ore (sample P698A) in the Mushgia Khudag hydrothermal deposits, Mongolia. The matrix is composed of microscale crystals of quartz, goethite, phlogopite, apatite, monazite and celestine.

We first apply the model to the rock composed of only two minerals as the simplest example. Figure 1b shows the microphotograph of a fluorite-hematite ore (sample P02) formed through hydrothermal activity related to the Bushveld granite, South Africa. A mass balance relationship between mineral and whole-rock composition (see general form in Eq. (2)) can be expressed as:

$$\begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} Hem \\ Fl \end{pmatrix} = \begin{pmatrix} Fe \\ Ca \end{pmatrix} \quad (6)$$

where each element symbol shows molecular proportion of the element. The compositional matrix in the left-hand side is based on the chemical formula listed in Table 1. By substituting whole-rock element compositions and by premultiplying the inverse of compositional matrix, Eq. (6) can be rewritten as:

$$\begin{pmatrix} Hem \\ Fl \end{pmatrix} = \begin{pmatrix} 0.5 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0.811 \\ 0.384 \end{pmatrix} \quad (7)$$

The results of the norm calculation with the propagation of chemical analysis error are shown in Table 2 (The molecular ratios are converted into wt% and vol % using parameters listed in Table 1). The results of the modal analysis by point-counting are also shown for comparison. The point-count data are collected as 30 sets of $N = 36$ and the associated error is estimated in terms of the sample standard deviation following the scheme of Neilson and Brockman (1977). It should be noted that the chemical analysis error depends on many factors and vary from laboratory to laboratory, whereas there is no interlaboratory difference in the modal analysis using same stochastic model. The calculated volume percent of normative minerals (hematite and fluorite) agree with the modal analysis data within the margin of the modal analysis error.

A second example is the application of the calculation to a rock containing both magnetite and hematite: a holocrystalline apatite ore (sample P700D) formed through hydrothermal activity related to the intrusion of syenite, Mushgia Khudag, Mongolia (Fig. 1a and c). We used the r value of 1 ± 0.1 and took into account its error as well as the chemical analysis error. The mass balance relationship between mineral and whole-rock composition can be expressed as:

$$\begin{pmatrix} 5 & 0 & 0 & 0 \\ 0 & 4.04 & 0 & 6 \\ 0 & 0 & 6 & 0 \\ 0 & 0 & 2 & 2 \end{pmatrix} \begin{pmatrix} Ap \\ Mag + Hem \\ Phl \\ Ann \end{pmatrix} = \begin{pmatrix} Ca \\ Fe \\ Mg \\ K \end{pmatrix} \quad (8)$$

The composition of the phlogopite crystal in Fig. 1c can be described by mixing of two end-members, phlogopite and annite (Table 1). By substituting whole-rock element compositions and by premultiplying the inverse of compositional matrix, Eq. (8) can be rewritten as:

$$\begin{pmatrix} Ap \\ Mag + Hem \\ Phl \\ Ann \end{pmatrix} = \begin{pmatrix} 0.2 & 0 & 0 & 0 \\ 0 & 0.248 & 0.248 & -0.743 \\ 0 & 0 & 0.167 & 0 \\ 0 & 0 & -0.167 & 0.5 \end{pmatrix} \begin{pmatrix} 0.637 \\ 0.210 \\ 0.011 \\ 0.007 \end{pmatrix} \quad (9)$$

The results of the calculation are shown in Table 3. All mineral volumes calculated by the present norm calculation agree with those determined by the point-counting method within the analytical errors.

The present norm calculation can be applied to the rocks whose constituent minerals are too small to conduct point-counting analysis. Figure 1d shows the microphotograph of a porphyritic apatite ore (sample P698A) formed through hydrothermal activity related to the activity of syenite, Mushgia Khudag, Mongolia. The rock is composed of large crystals of fluorapatite, phlogopite and goethite, and microscale crystals of quartz, goethite, phlogopite, fluorapatite, monazite and celestine. The point-counting method is not available for the microscale matrix. The mass balance relationship between mineral and whole-rock composition can be expressed as:

$$\begin{pmatrix} 1 & 0 & 6 & 6 & 0 & 0 & 0 \\ 0 & 1 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} Qtz \\ Goe \\ Phl \\ Ann \\ Ap \\ Mnz \\ Cel \end{pmatrix} = \begin{pmatrix} Si \\ Fe \\ Mg \\ K \\ Ca \\ P \\ Sr \end{pmatrix} \quad (10)$$

By substituting whole-rock element compositions and by premultiplying the inverse of compositional matrix, Eq. (10) can be rewritten as:

$$\begin{pmatrix} Qtz \\ Goe \\ Phl \\ Ann \\ Ap \\ Mnz \\ Cel \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & -3 & 0 & 0 & 0 \\ 0 & 1 & 1 & -3 & 0 & 0 & 0 \\ 0 & 0 & 0.167 & 0 & 0 & 0 & 0 \\ 0 & 0 & -0.167 & 0.5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -0.6 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0.308 \\ 0.031 \\ 0.018 \\ 0.008 \\ 0.669 \\ 0.402 \\ 0.015 \end{pmatrix} \quad (11)$$

The results of the calculation are shown in Table 4. The normative volume abundance for each crystal includes the crystal volume in the matrix. The relatively lower volume abundances of the point-counted crystals seem to be caused by the loss of counts in the microscale matrix. Prospects of ore generally contain the micro-scale minerals that are enriched in efficient elements. This norm calculation method would become a powerful tool to estimate proportion of ore minerals whose size is too small for point-counting analysis.

Table 3 Comparison between normative and modal abundance of minerals in holocrystalline apatite ore (sample P700D)

Mineral	Norm (wt %)	Norm* (vol %)	Mode (vol %)
Fluorapatite	64.24 ± 0.50	82.88 ± 0.65	80.74 ± 1.76
Magnetite + Hematite	15.65 ± 0.27	12.48 ± 0.22	13.89 ± 1.49
(Magnetite)	7.77 ± 0.26	6.23 ± 0.21	7.04 ± 0.80
(Hematite)	7.88 ± 0.27	6.26 ± 0.22	6.85 ± 0.69
Phlogopite + Annite	3.34 ± 0.33	4.63 ± 0.46	5.37 ± 1.06
(Phlogopite)	1.59 ± 0.05	2.20 ± 0.07	-
(Annite)	1.75 ± 0.28	2.43 ± 0.39	-

* Volume percentages are normalized to total 100 % for comparison with modal analysis

Table 4 Comparison between normative and modal abundance of minerals in porphyritic apatite ore (sample P698A)

Mineral	Norm (wt %)	Norm* (vol %)	Mode (vol %)
Quartz	17.10 ± 0.30	21.71 ± 0.39	matrix
Goethite	2.30 ± 0.24	1.80 ± 0.19	1.67 ± 0.45
Phlogopite + Annite	3.34 ± 0.54	3.76 ± 0.61	3.33 ± 0.45
(Phlogopite)	2.48 ± 0.13	2.79 ± 0.15	-
(Annite)	0.86 ± 0.41	0.97 ± 0.46	-
Fluorapatite	67.48 ± 0.12	70.27 ± 0.13	66.02 ± 2.26
Monazite-(Ce)	0.23 ± 0.33	0.15 ± 0.22	matrix
Celestine	2.73 ± 0.00	2.32 ± 0.00	matrix

* Volume percentages are normalized to total 100 % for comparison with modal analysis

Acknowledgements

K.N., Y.W. and T.T. thank to E. L. Tongu, S. Foya, N. S. Mayekiso, R. Yoshikawa and S. Kodama for the collaborative sampling of the fluorite-hematite ore in South Africa. Discussions with T. Ikeda contributed substantially to the content of this paper. This work was supported by a Grant-in-Aid for Young Scientists (B) (21740377) from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT KAKENHI).

References

- Cox, K. G., Bell, J. D. and Pankhurst, R. J. (1979) *The Interpretation of Igneous Rocks*. Allan & Unwin, London, 450p.
- Cross, C. W., Iddings, J. P., Pirsson, L. V. and Washington, H. S. (1902) A quantitative chemico-mineralogical classification and nomenclature of igneous rocks. *J. Geol.*, 10, 555–690.
- Deer, W.A., Howie, R.A. and Zussman, J. (1992) *An Introduction to the Rock Forming Minerals* (2nd ed.), Longman Scientific and Technical Publications, London, 696p.
- Johannsen, A. (1931) *A Descriptive Petrography of the Igneous Rocks*. vol. 1, Chicago University Press, 267p.
- Kelsey, C. H. (1965) Calculation of the C. I. P. W. norm. *Mineral. Mag.*, 34, 276–282.
- Le Maitre, R. W. (1976) Some problems of the projection of chemical data into mineralogical classifications. *Contrib. Mineral. Petrol.*, 56, 181–189.
- Middlemost, E. A. K. (1989) Iron oxidation ratios, norms and the classification of volcanic rocks. *Chem. Geol.*, 77, 19–26.
- Neilson, M. J. and Brockman, G. F. (1977) The error associated with point-counting. *Am. Mineral.*, 62, 1238–1244.
- Nishimura, K. and Yanagi, T. (2000) In situ crystallization observed in the Osumi granodiorite batholith, *Earth Planet. Sci. Lett.*, 180, 185–199.
- Pruseth, K. L. (2009) MATNORM: Calculating NORM using composition matrices. *Comput. Geosci.*, 35, 1785–1788.
- Ragland, P. C. (1989) *Basic Analytical Petrology*. Oxford University Press, Oxford, 369p.
- Verma, S. P., Torres-Alvarado, I. S. and Sotelo-Rodríguez, Z. T. (2002) SINCLAS: standard igneous norm and volcanic rock classification system. *Comput. Geosci.*, 28, 711–715.
- Washington, H. S. (1917) *Chemical analyses of igneous rocks*. US Geological Survey Professional Paper, 99.

要旨

正方行列を用いた鉱物ノルム計算法：微小鉱石鉱物の鉱量評価にむけて

西村光史, 渡辺 寧, 実松健造, 星野美保子, 高木哲一

正方行列を用いて岩石試料の化学組成（全岩化学組成）から構成鉱物の体積比を見積も

る手法（ノルム計算法）を開発した。鉱物の種類と化学組成は既知のパラメータとして扱う。鉱物の体積比は全岩の $\text{FeO}/\text{Fe}_2\text{O}_3$ 比が分かっている場合でも計算可能である。本モデルをいくつかの完晶質の岩石に適用し、鉱物の体積比を計算したところ、ポイントカウントデータと極めてよく一致することが確認された。本モデルは原理的にすべての岩石種に適用することが可能である。鉱床中の鉱石鉱物には、しばしばポイントカウント分析ができないほど微小で少量のものが存在する。そのような場合、本研究のノルム計算法は鉱物の体積比を見積もる有力なツールとなりうる。