

MEASURING MINERAL ABUNDANCE IN SKARN. II. A NEW LINEAR PROGRAMMING FORMULATION AND COMPARISON WITH PROJECTION AND RIETVELD METHODS

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ABSTRACT

The problem of estimating mineral abundances from whole-rock compositions can be attacked with a formulation that allows the incorporation of theoretical and empirical data on the range of composition of the minerals. A change of variables allows this intrinsically nonlinear problem to be solved with standard linear programming techniques. Calculations based on bulk compositions of samples previously studied by the Rietveld method show very good agreement for major minerals. The results are superior to those obtained by a projection method that also uses bulk-composition data. Estimates of mineral abundances based on bulk-composition data can be obtained rapidly and inexpensively and provide a useful method for reconnaissance studies.

Keywords: modal analysis, linear programming, wollastonite, skarn.

SOMMAIRE

On peut résoudre le problème que présente la détermination de l'abondance des minéraux à partir de compositions globales de roches avec une formulation qui permet d'incorporer des données théoriques et empiriques à propos de l'intervalle de composition des minéraux. Un changement de variables permet de résoudre ce problème fondamentalement non linéaire par des techniques standard de programmation linéaire. Des calculs à propos des minéraux majeurs, fondés sur la composition globale d'échantillons préalablement étudiés par la méthode de Rietveld, concordent très bien. La concordance est supérieure à celle obtenue avec une méthode de projection fondée aussi sur les compositions globales. L'estimation d'abondances de minéraux à partir des compositions globales, qui se fait rapidement et à coûts modestes, peut s'avérer utile dans les programmes de reconnaissance.

(Traduit par la Rédaction)

Mots-clés: analyse modale, programmation linéaire, wollastonite, skarn.

INTRODUCTION

The petrological and economic importance of determining mineral abundance in skarns has led to a number of methods of estimation. Because direct visual observation is in many cases difficult and expensive, alternative techniques have been developed. In the previous paper, Raudsepp *et al.* (1999) compared results obtained by X-ray-powder diffraction and Rietveld analysis with the predictions made by projecting bulk-composition data onto a set of phase and additive components. In this paper, we examine an alternative

procedure to estimate mineral abundances in the same suite of samples given bulk compositions and some information on the composition of the minerals. The results of all three methods are compared at the end of this paper.

This problem is a subset of the more general problem concerning mixtures, as reviewed by Renner *et al.* (1989) and Weltje (1997), in which the number and composition of end members of a mixture are inferred from a suite of bulk compositions alone. In the application discussed in this paper, the mixture is a rock, and the end members are compositions of model minerals.

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Unlike the general expression of the problem, the possible end-members are constrained to be a set of minerals of variable composition.

In its simplest form, the problem is as follows: given a set of compositions of n model minerals and a measured whole-rock composition, find the proportion of the minerals that best approximates the bulk composition. There must be a mass balance for each of the m constituents (commonly oxides) of the analyses. These mass balances can be expressed as a set of equations:

$$\sum_{j=1}^n a_{ij} x_j = b_i \quad i = 1, 2, \dots, m \quad (1)$$

$$x_j \geq 0, \quad j = 1, 2, \dots, n$$

where the constants a_{ij} are the amounts of constituent i in mineral j , the constants b_i are the amounts of constituent i in the bulk composition, and the unknowns x_j are the proportions of the minerals. The equations represent the mass-balance relationship of any conservative quantity. The inequalities reflect the fact that the proportions of model minerals in the solution must all be zero or positive quantities.

A general approach to constrained linear least-squares problems was outlined by Ghiorsio (1983). Recently, Metzner & Grimmeisen (1990) attacked the modal abundance problem with an iterative least-squares method using actual or assumed mineral and end-member compositions. With this approach, the number of mineral phases should not exceed about half of the analyzed elements, and the same end-member should not be used in more than one mineral. Because an unconstrained least-squares technique is employed, it is possible that negative modal abundances will be calculated. Laube *et al.* (1996) extended the method by using a combinatorial approach to find solutions in which only positive modal abundances occur. Their procedures include statistical weighting of the input data, a robust technique for regression, and calculation of maximum likelihood results. De Caritat *et al.* (1994) avoided the negative solution problem by using a linear programming technique to obtain modes of fine-grained sedimentary rocks. Rather than a least-squares minimization, their technique permits the minimization of a variety of linear objective functions.

FORMULATION OF THE PROBLEM

In many practical problems it is important that the model allow for the natural variability of mineral compositions in the rocks being studied. In other words, the values of a_{ij} in equations (1) are unknowns rather than constants, hence the m equations are nonlinear and may have as many as $(n + m \times n)$ unknowns. The variability may be known empirically from results of chemical analyses of the minerals or theoretically from crystallo-

graphic and thermodynamic considerations. Our approach features a change of variables that allows the problem to be solved by linear programming and permits empirical compositions and stoichiometric properties of the minerals to be used to constrain the unknown compositions of the minerals.

In our formulation, the unknowns are x_j , the n values of the weight fractions of model minerals and y_i^j , the $m \times n$ values of the variables (weight percent of oxide i in mineral $j \times$ weight fraction of mineral j). Weight fractions of the minerals are thus determined directly, whereas the compositions of individual mineral are determined after the solution is obtained by dividing the appropriate weight fraction \times weight percent by the computed weight fraction, *i.e.*, the weight percent of oxide i in mineral j is y_i^j/x_j . With this number of unknowns, the m mass-balance relationships (1) are insufficient to provide unique solutions. This problem is overcome by specifying inequality constraints corresponding to various known properties of the model minerals. The numerical technique used to solve such sets of equations and inequalities is linear programming.

Beginning with the seminal work of Greenwood (1967), linear programming has been applied in petrological mass-balance problems for a number of years (*e.g.*, Wright & Doherty 1970, Banks 1979, Gordon *et al.* 1991, de Caritat *et al.* 1994). In this technique, a set of inequalities, rather than equations, are used to constrain the values of the unknowns. Instead of a unique solution, the method finds the minimum or maximum value of a linear combination of variables. Mathematically, the linear programming problem is:

$$\min(\max) \sum_{j=1}^n \lambda_j x_j$$

subject to:

$$\sum_{j=1}^n a_{ij} x_j \leq b_i \quad i = 1, 2, \dots, m \quad (2)$$

$$x_j \geq 0, \quad j = 1, 2, \dots, n$$

In this notation, the symbols a_{ij} and b_i now refer to arbitrary quantities which constrain the solution. The

function $\sum_{j=1}^n \lambda_j x_j$ is called the *objective function*, whereas the equations and inequalities are the *constraints*. Such problems may be *feasible*, in which case a minimum or maximum value of the objective function can be obtained, *infeasible*, in which case the constraints admit no solution, or *unbounded*, in which case the constraints fail to restrict the objective function to a finite value. The structure of the problems addressed in this study and the nature of unknowns x_j and quantities λ_j , a_{ij} , and b_j are discussed below.

CONSTRAINTS

Mass-balance constraints

In the notation used here, equations (1) become:

$$\sum_{j=1}^n y_i^j = b_i \quad i = 1, 2, \dots, m$$

$$y_i^j \geq 0, \quad i = 1, 2, \dots, m; j = 1, 2, \dots, n \quad (3a)$$

If the measured bulk-compositions b_i are not known exactly, but lie within a known range $\pm \delta b_i$, equations (3a) can be expanded to:

$$\sum_{j=1}^n y_i^j \leq (b_i + \delta b_i) \quad i = 1, 2, \dots, m$$

$$-\sum_{j=1}^n y_i^j \leq -(b_i - \delta b_i) \quad i = 1, 2, \dots, m \quad (3b)$$

$$y_i^j \geq 0, \quad i = 1, 2, \dots, m; j = 1, 2, \dots, n$$

There will be $2 \cdot m$ constraints of this type.

Mathematical constraints

The main mathematical constraint is that the sum of the n weight fractions of model minerals should total 1. This constraint can be expressed as the equality $\sum_{j=1}^n x_j = 1$. Alternatively, this constraint can be expressed as two inequalities:

$$\sum_{j=1}^n x_j \leq 1$$

$$-\sum_{j=1}^n x_j \leq -1 \quad (4a)$$

The latter formulation can then be extended to allow the sum to vary within the number of significant digits in the data, for example:

$$\sum_{j=1}^n x_j \leq 1.001$$

$$-\sum_{j=1}^n x_j \leq -0.999 \quad (4b)$$

There will be two constraints of this type.

Constraints on mineral compositions I: totals

The composition of each mineral expressed in oxide weight percent should total exactly 100 in the case of pure minerals or end-members of solid solutions. If compositions are known exactly, this condition can be written

$$\sum_{i=1}^m y_i^j = 100 x_j$$

or

$$100 x_j - \sum_{i=1}^m y_i^j = 0 \quad j = 1, 2, 3 \dots n \quad (5a)$$

In the case of minerals with measured compositions, the total should lie within an acceptable range ($100 \pm \varepsilon_j$), and these constraints may be expressed as:

$$(100 - \varepsilon_j) \cdot x_j - \sum_{i=1}^m y_i^j \leq 0$$

$$-(100 + \varepsilon_j) \cdot x_j + \sum_{i=1}^m y_i^j \leq 0 \quad j = 1, 2, 3 \dots n \quad (5b)$$

There will a pair of inequalities for each model mineral, giving a total of $2 \cdot n$ constraints of this type.

Constraints on mineral compositions II: individual oxides

The permitted variation in the weight percent of oxide j in model mineral i (a_{ij}) can be specified using inequalities analogous to (5b), where the compositional range is $a_{ij} \pm \delta a_{ij}$.

$$(a_{ij} - \delta a_{ij}) \cdot x_j - y_i^j \leq 0$$

$$-(a_{ij} + \delta a_{ij}) \cdot x_j + y_i^j \leq 0 \quad (6)$$

There may be as many as m pairs of such inequalities for each mineral, hence a maximum of $2 \cdot m \cdot n$ inequalities of this type for any particular problem.

Explicit crystallographic constraints

Crystallographic or site-occupancy constraints are specific to individual minerals or mineral groups. If the compositions of particular minerals can be adequately modeled by a mixture of theoretical end-members, then the compositions of these end members can be used in the formulation of the problem instead of empirical compositions (e.g., Metzner & Grimmeisen 1990, de Caritat *et al.* 1994, Laube *et al.* 1996). This procedure essentially collapses inequalities (5) and (6) to equations for the theoretical end-members chosen. The weight fraction of the mineral solution is then the sum of the weight fractions of the individual end-members.

Cation-ratio constraints

It is not always feasible to express compositions of natural minerals as mixtures of end members, in particular where only partial results of chemical analyses are available. However, in some problems, the model minerals may have a fixed ratio of particular cations that should be respected in the calculations. An example would be the requirement that in a garnet the cation ratio $[\text{Si} + \text{Al} + \text{Fe}^{3+} + \text{Ti}]:[\text{Mg} + \text{Fe}^{2+} + \text{Mn} + \text{Ca}]$ be 10:6.

In order to apply such a constraint, the variables y_i^j must be scaled to cation numbers. The form of such a constraint would then be:

$$\sum_{\text{site1}} y_i^j \frac{c_i}{m_i} - k \cdot \sum_{\text{site2}} y_i^j \frac{c_i}{m_i} = 0 \quad (7a)$$

where c_i is the number of moles of cation per mole of oxide i , m_i is the molecular weight of oxide i , and k is the ratio of cations on site 1 to cations on site 2. If the ratio is allowed to vary between $k - \delta k$ and $k + \delta k$, the equation can be replaced with two inequalities.

$$\begin{aligned} \sum_{\text{site1}} y_i^j \frac{c_i}{m_i} - (k + \delta k) \cdot \sum_{\text{site2}} y_i^j \frac{c_i}{m_i} &\leq 0 \\ -\sum_{\text{site1}} y_i^j \frac{c_i}{m_i} + (k - \delta k) \cdot \sum_{\text{site2}} y_i^j \frac{c_i}{m_i} &\leq 0 \end{aligned} \quad (7b)$$

OBJECTIVE FUNCTION

Any linear combination of variables can be used as the objective function (function to be minimized or maximized). In the context of this formulation, an obvious choice is to determine the minimum and maximum weight fraction of particular minerals in the model system.

An alternative formulation, mentioned here for completeness, can be obtained by the inclusion of an additional set of $2 \cdot m$ explicit slack variables that provide the amount by which each mass-balance equation is violated (e.g., Gordon *et al.* 1991, de Caritat *et al.* 1994). The objective function to be minimized in this formulation is the sum of these variables. This type of objective function has the advantage that a mass-balance solution is guaranteed. The values of the explicit slack variables show which oxides fail to balance exactly. This information can be interpreted in geological terms and used to identify sources of inconsistency in the model.

APPLICATION OF THE LINEAR PROGRAMMING METHOD

This methodology has been applied to a set of 20 samples of wollastonite skarn from the Isk deposit of northwestern British Columbia (Jaworski & Dipple 1996a). The samples were crushed and homogenized

two-meter intervals of drill core. The sample size means that an individual sample may contain several rock types, and the formulation must then allow for the occurrence of any of the minerals observed in the area.

Bulk compositions

Bulk chemical compositions were determined by X-ray fluorescence spectroscopy on splits of the same powdered rock material that was used for X-ray powder diffraction (Raudsepp *et al.* 1999). The bulk chemical compositions are shown in Table 1. Relative uncertainties in these analytical results provided by the assay company are shown in Table 2.

Model minerals

On the basis of the work of Jaworski (1996) and Jaworski & Dipple (1996a, b), the most abundant minerals in the samples are wollastonite, quartz, calcite, hydroxylapatite, K-feldspar, titanite, augite, grossular and andradite. Electron-microprobe data exist for wollastonite, titanite, augite, grossular and andradite in skarns in the area (M. Raudsepp, unpubl. data).

Total iron was recalculated to FeO. The model compositions for quartz, calcite, hydroxylapatite, K-feldspar and diopside were taken as those of theoretical pure phases. For model calcite and apatite, LOI was computed as weight % CO_2 and H_2O , respectively. The value of weight % of each oxide and the total weight % of model wollastonite, titanite, augite, grossular and andradite were constrained to lie between the maximum and minimum values obtained in the electron-microprobe analyses. The minerals used in the calculations and the bounds on individual oxide weight % are shown in Tables 3, 4 and 5.

Objective functions

The objective functions were chosen to maximize and minimize the weight fraction of wollastonite, the ore mineral in the skarn deposit.

Algorithm

Computations were carried out with the linear programming function LP of the Optimization Toolbox, part of the Matlab system distributed by The MathWorks, Inc. of Natick, Massachusetts.

RESULTS

The calculated weight % and mole % mineral abundances for 16 samples are shown in Tables 6 and 7. Molecular weights were computed on the basis of two atoms of oxygen per mole in quartz, three per mole in wollastonite and calcite, five per mole in titanite, six per mole in diopside and augite, eight per mole in K-feld-

TABLE 1. WHOLE-ROCK CHEMICAL COMPOSITIONS, WOLLASTONITE SKARN, ISK DEPOSIT, BRITISH COLUMBIA

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
3810	50.91	0.03	0.55	0.80	0.09	0.71	45.94	0.23	0.12	0.01	0.57	99.96
2760	50.33	0.07	1.64	0.93	0.07	0.79	44.96	0.22	0.32	0.01	0.47	99.81
420	49.63	0.12	2.36	1.49	0.07	0.99	44.17	0.16	0.16	0.03	0.75	99.93
2610	49.28	0.15	2.08	2.08	0.10	1.19	43.65	0.27	0.23	0.02	0.84	99.89
4820	48.92	0.32	1.77	3.10	0.11	1.95	42.24	0.16	0.12	0.06	1.01	99.76
1270	47.79	0.16	4.67	2.19	0.07	1.59	42.03	0.31	0.22	0.05	0.65	99.73
3395	46.17	1.57	1.77	4.71	0.14	1.87	40.52	0.49	0.29	0.49	1.76	99.78
5795	50.00	0.20	2.03	3.09	0.11	4.36	38.41	0.20	0.25	0.03	0.99	99.67
2595	47.79	0.68	2.76	6.62	0.17	3.83	35.86	0.42	0.40	0.15	0.44	99.12
6360	32.55	0.13	2.35	2.02	0.08	3.20	42.97	0.41	0.46	0.01	15.74	99.92
3600	46.31	0.73	5.04	6.47	0.19	2.48	33.41	0.41	1.41	0.18	2.79	99.42
360	47.45	0.94	2.88	8.04	0.18	5.76	32.27	0.38	0.56	0.56	0.75	99.77
5195	44.46	0.27	2.03	9.18	0.35	7.94	26.87	0.34	0.24	0.35	7.73	99.76
2795	49.36	0.42	2.36	7.14	0.16	11.25	24.58	0.79	0.71	1.58	1.28	99.63
4995	49.30	0.75	2.81	11.65	0.46	8.72	23.41	0.56	0.88	0.42	0.32	99.28
2995	49.27	0.51	2.56	7.04	0.16	10.84	24.10	0.99	0.90	1.77	1.47	99.61
3470	49.58	0.34	4.92	3.65	0.13	1.13	35.29	0.52	2.56	0.05	1.43	99.60
4400	53.03	0.43	9.85	4.40	0.13	2.55	20.90	1.66	4.46	0.31	1.42	99.14
5000	54.00	0.14	12.76	2.22	0.11	0.66	19.01	2.49	5.12	0.06	2.57	99.14
5270	49.58	0.14	1.19	1.78	0.11	0.97	44.29	0.41	0.25	0.03	1.04	99.79

The bulk compositions are reported in weight %. LOI: loss on ignition.

TABLE 2. RELATIVE ERRORS (%) ASSOCIATED WITH WHOLE-ROCK COMPOSITIONS

SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
0.0038	0.0203	0.0153	0.0087	0.0588	0.0081	0.014	0.0327	0.0253	0.0734	0.05

TABLE 3. WEIGHT % OXIDES IN MODEL MINERALS WITH FIXED COMPOSITIONS

	Qtz	Cal	Ap	Kfs	Di
SiO ₂	100	0	0	64.76	55.49
TiO ₂	0	0	0	0	0
Al ₂ O ₃	0	0	0	18.32	0
FeO	0	0	0	0	0
MnO	0	0	0	0	0
MgO	0	0	0	0	18.61
CaO	0	56.03	55.82	0	25.90
Na ₂ O	0	0	0	0	0
K ₂ O	0	0	0	16.92	0
P ₂ O ₅	0	0	42.39	0	0
LOI	0	43.97	1.79	0	0

spar, twelve per mole in grossular and andradite, and twelve per mole in apatite on an anhydrous basis.

Feasible solutions were obtained for all but four of the samples previously studied (Raudsepp *et al.* 1999). Three of these (3470, 4400 and 5000) had anomalously high contents of K-feldspar (> 14 wt%), possibly reflecting the presence of minerals not included in the model. The lack of a solution for sample 5270 is enigmatic.

TABLE 4. MINIMUM WEIGHT % LIMITS FOR MODEL MINERALS WITH VARIABLE COMPOSITIONS*

	Wc	Ttn	Aug	Grs	Adr
SiO ₂	51.09	30.15	50.39	64.76	33.21
TiO ₂	0	37.12	0	0	1.08
Al ₂ O ₃	0	0.42	0.03	18.32	1.13
FeO	0.03	1.19	5.81	0	17
MnO	0	0	0	0	0.01
MgO	0.03	0	10.42	0	0.11
CaO	47.33	28.03	20.34	0	32.52
Na ₂ O	0	0.05	0.16	0	0
K ₂ O	0	0	0	16.92	0
P ₂ O ₅	0	0	0	0	0
LOI	0	0.22	0	0	0
Total	98.9	97.47	97.3	96.5	96.65

* Columns do not correspond to actual results of analyses.

TABLE 5. MAXIMUM WEIGHT % FOR MODEL MINERALS WITH VARIABLE COMPOSITIONS*

	Wc	Ttn	Aug	Grs	Adr
SiO ₂	52.73	30.32	52.42	38.7	35.58
TiO ₂	0.06	38.02	0.31	0.06	5.46
Al ₂ O ₃	0.06	0.76	1.66	23.03	6.65
FeO	0.53	1.51	12.69	0.5	25.44
MnO	0.2	0	0.47	0.05	0.14
MgO	0.31	0.02	14.95	0.02	0.49
CaO	48.35	28.37	25.02	37.23	33.61
Na ₂ O	0.11	9	2.12	0	0.22
K ₂ O	0	0.01	0	0	0
P ₂ O ₅	0	0	0	0	0
LOI	0	0.29	0	0	0
Total	101.3	100.01	100.01	100.01	100.01

* Columns do not correspond to actual results of analyses.

TABLE 6. COMPUTED WEIGHT % MINERALS IN SAMPLES OF WOLLASTONITE ORE

Sample	3810	2760	420	2610	4820	1270	3395	5795	2595	6360	3600	360	5195	2795	4995	2995
Minimum wollastonite																
Wollastonite	86.26	80.72	73.07	70.73	63.04	57.03	50.34	48.10	33.27	21.81	21.59	14.58	0.00	0.00	0.00	0.00
Quartz	1.35	0.72	1.02	0.57	0.31	0.00	0.63	0.85	0.00	0.84	3.60	1.31	5.48	0.58	0.00	1.22
Calcite	1.36	1.12	1.79	2.00	2.41	1.55	4.14	2.36	1.04	37.59	6.64	1.73	16.67	2.62	0.76	3.01
Apatite	0.03	0.03	0.08	0.05	0.15	0.13	1.24	0.08	0.38	0.03	0.46	1.42	0.77	3.58	0.85	3.94
K-feldspar	0.69	1.84	0.92	1.32	0.69	1.27	1.67	1.44	2.30	2.65	8.12	3.23	1.45	4.30	4.94	5.45
Titanite	0.00	0.00	0.00	0.00	0.00	0.00	1.58	0.00	0.00	0.00	0.00	0.00	0.00	0.87	0.00	1.10
Diopside	0.00	0.00	0.00	0.00	0.00	0.33	0.00	10.53	2.14	6.28	0.00	15.14	0.00	19.52	0.00	17.64
Augite	6.61	7.39	9.33	11.25	18.61	14.57	17.75	23.18	32.95	19.64	23.71	28.38	68.21	63.49	83.16	62.94
Grossular	1.87	5.91	9.89	8.17	7.17	20.13	3.94	7.83	9.81	8.41	15.35	9.22	1.04	4.57	0.00	4.14
Andradite	1.38	1.83	3.45	5.45	7.18	5.07	18.58	5.39	17.94	3.20	20.47	25.44	5.92	0.00	10.74	0.12
Maximum wollastonite																
Wollastonite	91.62	87.13	83.21	81.09	76.29	68.41	60.09	63.59	52.81	35.94	39.30	39.08	5.87	12.27	6.80	11.20
Quartz	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.05	0.00	0.00	3.27	0.38	5.60	0.80	0.00	3.13
Calcite	1.23	1.01	1.62	1.81	2.17	1.40	3.75	2.14	0.93	35.32	6.01	1.56	16.67	2.62	0.65	3.01
Apatite	0.02	0.02	0.07	0.04	0.13	0.11	1.07	0.07	0.33	0.02	0.39	1.22	0.77	3.45	0.85	3.87
K-feldspar	0.69	1.84	0.97	1.32	0.73	1.27	1.67	1.51	2.42	2.65	8.54	3.39	1.45	4.30	4.94	5.45
Titanite	0.00	0.00	0.14	0.11	0.43	0.25	1.89	0.18	1.24	0.13	1.00	1.65	0.13	0.45	1.20	0.71
Diopside	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.92	0.00	0.00	0.00	0.00	0.00	0.00
Augite	5.74	5.52	5.22	7.95	12.06	10.51	17.78	27.60	28.85	16.84	19.28	41.01	67.31	74.38	83.27	71.69
Grossular	1.15	4.92	8.52	6.62	5.00	17.82	0.90	5.31	5.44	6.63	9.76	4.56	2.65	1.26	1.84	1.39
Andradite	0.00	0.00	0.71	1.50	3.14	0.69	13.31	0.00	7.54	0.00	12.00	6.74	0.00	0.00	0.00	0.00

RIETVELD METHOD

Raudsepp *et al.* (1999) applied the Rietveld method and a projection method to determine mineral abundances in these samples of wollastonite skarn. The Rietveld method uses X-ray powder-diffraction to characterize a sample. The structural parameters of each constituent mineral, together with experimental parameters, are refined by least-squares procedures to minimize the difference between observed and calculated powder-diffraction patterns. The result is a single estimate of mineral abundance for each of the skarn samples studied here. Raudsepp *et al.* (1999) evaluated the accuracy of the method by analyzing synthetic skarn that consisted of pre-weighed mixtures of skarn minerals. They concluded that the Rietveld method provides the best estimate of mineral abundance in natural skarn samples for minerals present in moderate to large abundance ($\geq 5\%$) but that it does not accurately measure the abundance of minerals present at lower concentrations.

PROJECTION METHOD

The projection method employs a basis transformation to convert whole-rock compositions in terms of oxides to molar abundances of additive and exchange components (Thompson 1982, Raudsepp *et al.* 1999). The whole-rock chemical compositions used by Raudsepp *et al.* (1999) are the same as in this study. The projection method determines mineral abundance but not mineral composition. This analysis for the Isk

wollastonite skarn is underdetermined: the abundances of calcite, K-feldspar, apatite and titanite are determined uniquely; abundances of wollastonite, quartz, pyroxene and garnet are constrained to lie between minimum and maximum values. An added complication for samples of the Isk skarn is that the number of substitution mechanisms must be reduced in order to obtain a feasible solution by the projection method. These simplifications introduce errors into the estimates of mineral abundance, although generally on the order of only a few mole percent. For example, although garnet contains Ti and pyroxene contains Na and K, the formulation of the projection technique employed by Raudsepp *et al.* (1999) restricted Ti to titanite, and Na and K to feldspar. As a result, the projection method overestimates the abundance of both titanite and feldspar in the skarn samples. Sensitivity analysis has confirmed that these simplifications do not adversely affect estimates of wollastonite abundance. The main source of inaccuracy in the projection method stems from the inability of the method to limit the range of compositional variability of individual mineral species.

DISCUSSION

Mineral abundances determined by linear programming, Rietveld analysis and projection techniques are compared in Figures 1, 2 and 3. The data are presented in Table 7. The linear programming results for wollastonite, total garnet, total pyroxene, quartz, calcite and feldspar are consistent with and bracket the Rietveld

TABLE 7. MINERAL ABUNDANCES IN MOLE %, WOLLASTONITE SKARN

Sample	3810	2760	420	2610	4820	1270	3395	5795	2595	6360	3600	360	5195	2795	4995	2995	
Wollastonite																	
Rietveld	93.73	89.75	87.67	86.01	81.81	79.03	73.42	69.88	63.49	42.18	47.75	40.98	1.10	0.78	0.76	0.76	
Proj. min ¹	93.89	92.75	86.76	86.64	78.08	80.87	73.13	60.27	54.45	29.45	39.82	24.27	0.00	0.00	0.00	0.00	
Proj. max ²	94.59	93.08	88.80	88.05	82.48	82.26	75.49	70.58	63.83	33.89	50.12	42.01	0.00	0.00	0.00	0.00	
LP ³ min	90.83	89.74	85.33	84.37	79.00	77.73	69.23	65.08	55.22	25.83	35.68	28.26	0.00	0.00	0.00	0.00	
LP max	94.87	93.52	91.84	90.19	86.23	84.67	76.16	77.05	71.91	39.89	54.71	57.56	8.14	20.89	12.75	18.22	
Pyroxene																	
Rietveld	3.41	3.57	4.71	5.67	8.50	7.49	8.71	20.43	24.68	10.48	13.23	36.82	47.61	86.49	85.69	83.13	
Proj. min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Proj. max	1.40	0.66	4.08	2.82	8.79	2.78	4.72	20.63	18.75	8.88	20.59	35.49	49.44	75.51	76.75	71.87	
LP min	3.61	4.26	5.65	6.95	12.05	10.52	12.63	23.83	30.22	16.01	20.30	44.12	52.05	83.53	88.30	79.48	
LP max	3.04	3.03	2.94	4.50	6.96	6.61	11.52	17.28	19.97	11.33	13.62	30.80	47.77	65.86	79.33	59.93	
Garnet																	
Rietveld	0.33	2.02	2.91	3.03	2.84	7.34	4.95	2.75	7.48	3.08	11.80	10.83	4.12	0.19	6.28	0.49	
Proj. min	1.13	2.95	3.47	4.37	3.80	9.99	6.94	3.16	9.96	4.46	8.06	11.17	0.00	6.04	9.69	5.82	
Proj. max	1.83	3.28	5.51	5.78	8.20	11.38	9.30	13.48	19.34	8.90	18.35	28.92	0.00	6.04	9.69	5.82	
LP min	0.83	2.14	3.84	3.93	4.31	8.55	7.24	4.33	10.83	3.40	14.05	15.59	2.38	2.27	5.16	2.07	
LP max	0.31	1.36	2.59	2.26	2.24	5.83	4.18	1.64	4.17	1.88	7.20	3.93	0.95	0.55	0.89	0.58	
Quartz																	
Rietveld	1.60	2.26	1.19	2.02	2.61	2.50	3.40	2.69	1.31	2.26	9.90	3.36	19.56	3.59	3.13	3.39	
Proj. min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	17.43	0.00	0.00	0.00	
Proj. max	1.40	0.66	4.08	2.82	8.79	2.78	4.72	20.63	18.75	8.88	20.59	35.49	17.43	0.00	0.00	0.00	
LP min	2.76	1.55	2.30	1.30	0.74	0.00	1.67	2.22	0.00	1.92	11.48	4.90	15.72	2.19	0.00	4.48	
LP max	0.00	0.00	0.00	0.00	1.04	0.00	0.00	0.11	0.00	0.00	8.81	1.09	15.05	2.65	0.00	9.81	
Calcite																	
Rietveld	0.54	0.58	2.11	2.32	2.96	2.41	4.62	3.03	1.06	40.15	10.58	2.88	24.91	0.29	0.06	0.17	
Projection	1.60	1.38	2.28	2.62	3.23	2.31	6.05	3.43	1.77	49.36	11.52	3.32	29.56	6.06	1.61	6.99	
LP min	1.66	1.45	2.42	2.77	3.49	2.44	6.60	3.70	1.99	51.52	12.72	3.89	28.69	5.91	1.84	6.65	
LP max	1.48	1.27	2.07	2.34	2.86	2.01	5.52	3.00	1.47	45.57	9.73	2.67	26.90	5.18	1.43	5.66	
Feldspar																	
Rietveld	0.26	1.62	1.21	0.93	0.78	0.70	0.37	0.99	0.63	1.56	5.33	2.22	0.82	2.83	2.22	4.17	
Projection	1.23	1.81	1.15	1.87	1.09	2.31	3.40	1.80	4.02	3.18	7.89	5.02	2.72	9.44	9.13	11.90	
LP min	0.30	0.86	0.45	0.66	0.36	0.72	0.96	0.81	1.60	1.31	5.59	2.60	0.90	3.49	4.29	4.34	
LP max	0.30	0.83	0.45	0.62	0.34	0.66	0.88	0.76	1.38	1.23	4.98	2.09	0.84	3.06	3.89	3.68	
Apatite																	
Rietveld	0.13	0.19	0.18	0.03	0.13	0.05	0.44	0.11	0.28	0.14	0.21	0.78	0.40	2.38	0.78	2.51	
Projection	0.01	0.01	0.02	0.01	0.04	0.04	0.36	0.02	0.13	0.01	0.15	0.55	0.28	1.73	0.49	1.94	
LP min	0.01	0.01	0.02	0.01	0.04	0.04	0.39	0.02	0.15	0.01	0.17	0.63	0.26	1.61	0.41	1.74	
LP max	0.01	0.01	0.02	0.01	0.03	0.03	0.31	0.02	0.10	0.01	0.13	0.42	0.25	1.36	0.37	1.45	
Titanite																	
Rietveld	0.00	0.01	0.03	0.02	0.39	0.46	4.11	0.12	1.08	0.15	1.20	2.16	1.48	1.73	1.08	2.65	
Projection	0.05	0.11	0.20	0.26	0.57	0.31	3.04	0.38	1.55	0.22	1.67	2.44	0.57	1.22	2.33	1.49	
LP min	0.00	0.00	0.00	0.00	0.00	0.00	1.28	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	1.24	
LP max	0.00	0.00	0.09	0.07	0.29	0.18	1.42	0.13	1.00	0.09	0.83	1.44	0.11	0.46	1.34	0.68	

¹ Min denotes calculation that minimizes wollastonite content, projection method. ² Max denotes calculation that maximizes wollastonite content, projection method. ³ LP is the linear programming method.

results (Fig. 1). Maximum and minimum abundances generally have a 5–10% range. This range decreases as mineral content increases, reflecting the fact that at high abundance, the bulk composition provides a major constraint on mineral abundances. The linear programming method systematically underestimates the abundances

of the minor minerals titanite and apatite relative to their concentration as determined by the Rietveld method (Figs. 1e, g).

Estimates of mineral abundance by the projection method also compare favorably with those of the Rietveld method (Fig. 2). Wollastonite, titanite and cal-

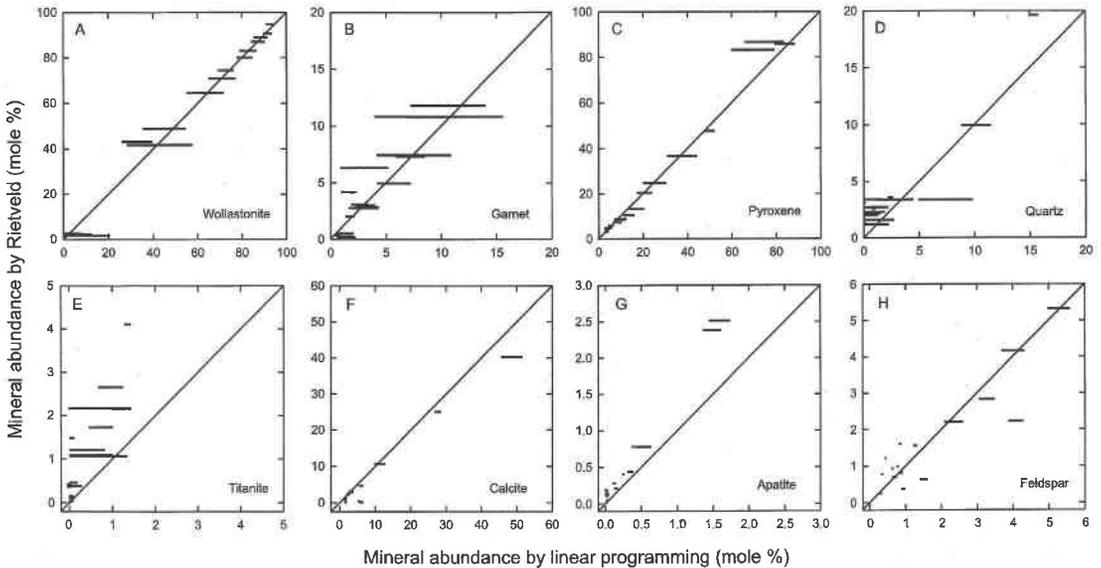


FIG. 1. Mineral abundance in mole % determined by linear programming *versus* mineral abundance determined by the Rietveld method. The length of the horizontal bars corresponds to the range of wollastonite contents obtained in the linear programming solution.

cite contents as determined by the two techniques are consistent; the projection method, however, tends to overestimate garnet and feldspar contents, and underestimate pyroxene and apatite abundance relative to the Rietveld method. The projection method results for quartz are consistent with the Rietveld results but with large brackets (Fig. 2d).

A comparison of the linear programming results with those of the projection method is instructive because both techniques use the same set of whole-rock chemical data (Table 1). This comparison (Fig. 3) shows excellent correlation for maximum and minimum abundances of wollastonite, calcite and apatite, and a clear tendency for the linear programming technique to estimate lower contents of garnet, titanite and feldspar with respect to the projection method.

The linear programming test was run to maximize and minimize wollastonite content, hence the range of wollastonite values is larger than the equivalent determination by the projection method. Calcite abundances estimated by the linear programming and projection techniques are very similar because both are constrained by the value of loss on ignition in the whole-rock analysis. This is sufficient to estimate the calcite content of the skarn samples (Figs. 1f, 2f), although direct measurement of CO_2 content of skarn would likely provide more accurate constraints on calcite content. The linear programming method systematically estimates higher abundances of pyroxene than the projection method, although the maximum pyroxene contents of the two

methods compare favorably. Quartz abundances as determined by the two methods are consistent, largely because of the extreme range in quartz content allowed by the projection method.

The linear programming method provides better estimates of pyroxene, garnet, quartz and feldspar content than the projection method because the linear programming technique incorporates a more accurate representation of mineral chemistry. The linear programming technique allows for all observed mechanisms of substitution within each mineral but limits their abundance to lie within the observed range of mineral compositions. This additional set of constraints is not included in the projection method. The projection method does not solve for the compositions of the minerals. Rather, it determines the extent of each substitution (exchange component) for the whole rock. This approach results in poor estimates of pyroxene and garnet abundance in the Isk skarn. For some solutions of the projection formulation, the total Mg content of the rock is accommodated by garnet through the Fe–Mg exchange vector (Figs. 2b,c). These solutions have zero pyroxene content. Garnet in the Isk skarn does not contain sufficient Mg to accommodate all of the Mg in the rock (Table 3). The linear programming solution for these samples requires non-zero pyroxene contents (Fig. 1c).

The projection and linear programming methods produce similar estimates of apatite abundance, both of which are determined by the P_2O_5 content of the rock. The discrepancy between Rietveld estimates of apatite

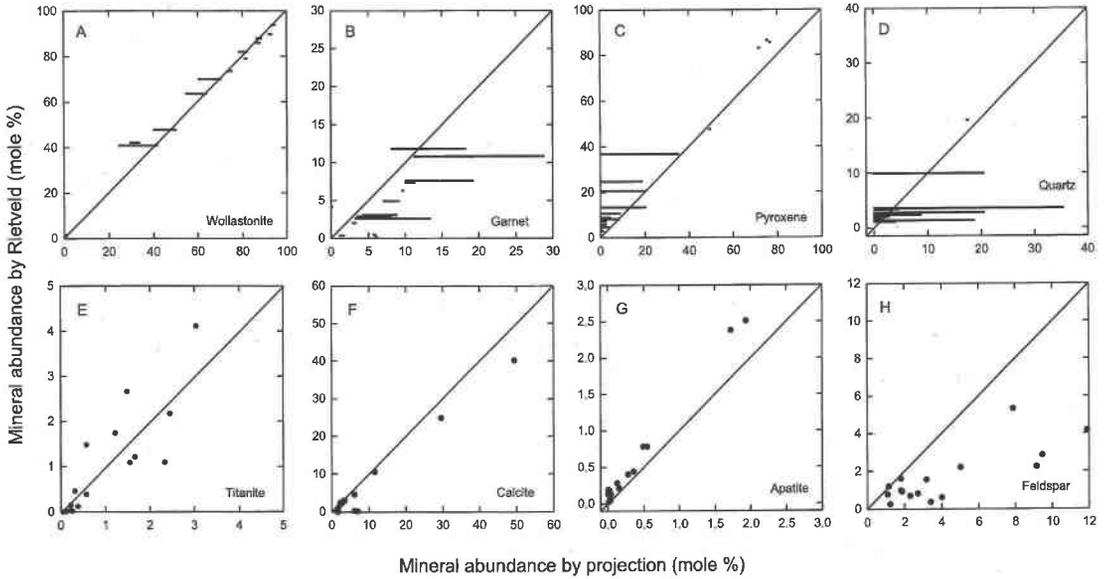


FIG. 2. Mineral abundance in mole % determined by projection *versus* mineral abundance determined by the Rietveld method. The length of the horizontal bars corresponds to the range of wollastonite contents obtained in the projection solution.

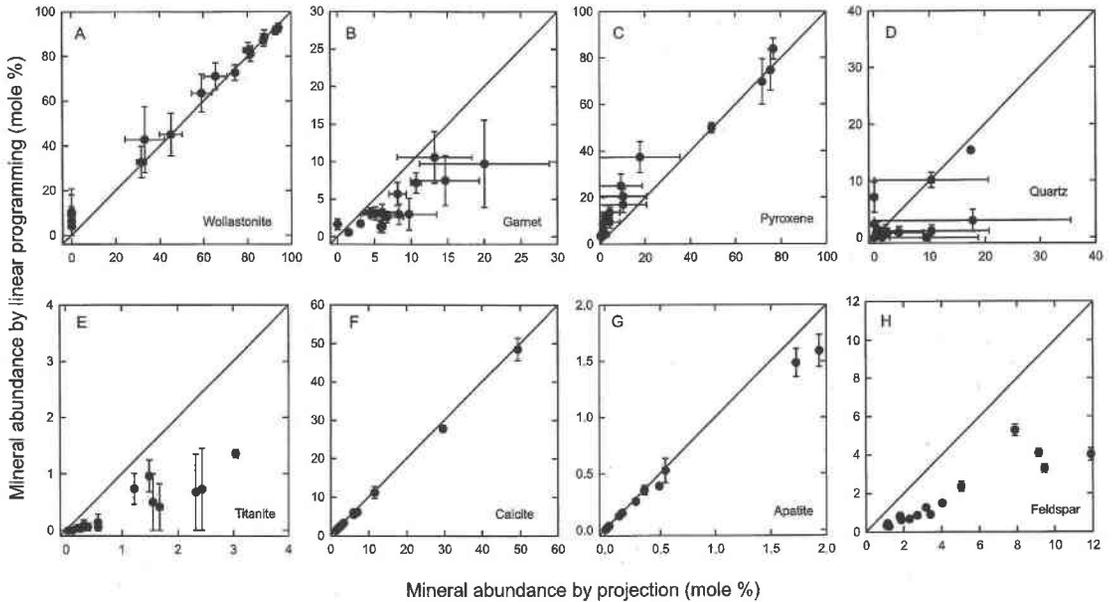


FIG. 3. Mineral abundance in mole % determined by the projection method *versus* mole % determined by the linear programming method.

content and those determined by linear programming and projection can be attributed to the inaccuracy of the Rietveld method for low-abundance minerals. Methods of estimation based on data on whole-rock composition provide more accurate determination of mineral abundance than the Rietveld method for minor phases that accumulate incompatible elements.

The results of this study show that the linear programming technique produces results in good agreement with the Rietveld method for the skarn samples in the reference dataset. The linear programming method is superior to the projection method for estimating mineral abundance in the complex calc-silicate skarn. Data required for the projection method are similar to those required for the linear programming method: bulk compositions and the nature of substitutions in the constituent minerals. The linear programming technique incorporates additional constraints, namely the range of substitutions. As a result, mineral abundances determined by linear programming are in general more accurate than those determined by projection. However, this does not translate into smaller computed ranges of wollastonite content. The extremes thus represent the most conservative and most optimistic grades of wollastonite ore. Bulk-composition methods, if augmented by mineralogical constraints, can provide rapid and inexpensive estimates of mineral abundances in skarns. The level of accuracy is sufficient for reconnaissance and exploration purposes.

ACKNOWLEDGEMENTS

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada (research grant to TMG and grant IOR195826 to GMD) and Whitegold Resources Inc. of Vancouver, B.C. We thank Bart Jaworski, Brian Lueck and Allen Achilles of Whitegold Resources for their continued support, and Howard Day and Andrew Zingg for their constructive comments.

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Received August 4, 1998, revised manuscript accepted January 25, 1999.