

Optimization of site occupancies in minerals using quadratic programming

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ABSTRACT

Atomic sites with multiple substituents are common in minerals, and correct site assignment of substituents in structure refinement is of fundamental importance. Substituents must be assigned to particular sites to fit the observed site scattering and chemical analysis, but the assignments are rarely made with mathematical rigor. We propose a quadratic programming approach to calculating optimal site assignments, thereby providing crystallographers with a mathematically robust starting point for the determination of site occupancies. Our program, OCCQP, implements this approach within the widely used *MATLAB* programming environment. User-defined weights may be assigned to the structural formula, site scattering, and bond-valence sums. The program is useful for evaluation of site occupancies in newly refined structures and re-evaluation of previously published structures with ad hoc site assignments.

INTRODUCTION

The assignment of site occupancies in structures with extensive substitutions is of fundamental interest in the characterization of geological and technological materials. For simple binary substitutions, in the absence of information such as spectroscopic data, the occupancies of fully occupied sites are (in theory) determined uniquely by inverse interpolation of either expected end-member bond lengths or site scattering of the two occupying species. With three or more substituents and the possibility of vacancies, simultaneous interpolation of both average bond length and mean atomic number yields infinitely many possible solutions. Traditionally this is resolved by making simplifying assumptions based on crystal-chemical reasoning. Hawthorne (1983) provides a comprehensive summary of the methods of characterization of site occupancies using crystallographic and spectroscopic data, and the reader is referred to that work for an excellent analysis of the problem and previous attempts at its solution. In particular, Hawthorne (1983) recognizes the appeal of a least-squares approach to site assignments, which is a method related to that described herein.

Even for binary substitutions, the situation is not entirely straightforward. For example, the decision to interpolate using site scattering instead of average bond lengths is tantamount to assigning infinite weight to the former and zero weight to the latter. Both types of data are significant, and both should be taken into consideration: the crystallographer will generally discard an assignment that gives an unreasonable fit for either measurement.

For larger problems, mineralogists incorporate additional information (e.g., spectroscopic analyses) and adjust site occupancies in an attempt to mimic observed bond lengths, site-scattering values, and quantitative chemical data. Rarely, however, are these adjustments made with mathematical rigor. They invariably incorporate simplifying assumptions based on crystal-chemical reasoning. Examples of such simplifications include substituting only species of like-valence at a site, assuming certain species cannot even be considered at a site, assuming only two species may occupy a site, and assuming certain sites are fully occupied.

We present a model for optimizing the occupancies of multiply occupied sites of crystals. The approach is based on crystal-structure data and chemical analyses of the compound, without making prior assumptions. Furthermore, this method provides a flexible means of evaluating the trade-off inherent in assigning occupancies on the basis of a single criterion, such as satisfying the observed structural formula exactly. Multiple criteria may be used and their relative importance adjusted interactively. The optimized occupancies obtained by this method provide a rigorous starting point for evaluation by crystallographers; the optimization yields excellent results from minimal assumptions.

THE METHOD OF OPTIMIZING OCCUPANCIES

Our formulation for assigning occupancies at multiply occupied sites makes use of the following theses, assuming perfectly observed values: (1) the sum of the occupancies of all substituents at a site will not exceed unity; (2) the sum of the occupancies of substituents times their respective site scattering will equal the observed mean scattering at each site; (3) the modeled chemical composition at all sites will sum to the observed chemical analysis. These relations are formalized below.

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We seek to determine those nonnegative values of the variables $x_k^{(j)}$ having $\sum_{k=1}^n x_k^{(j)} \leq 1$ for each site j , which satisfy the following equations:

$$\sum_{k=1}^n x_k^{(j)} Q_k = Q_{\text{obs}}^{(j)}, \text{ for each site } j; \quad (1)$$

$$\sum_{j=1}^m x_k^{(j)} C^{(j)} = C_k^{\text{obs}}, \text{ for each species } k. \quad (2)$$

Table 1 describes the notation used throughout this work.

Note that the equation

$$\sum_{k=1}^n Q_k C_k^{\text{obs}} = \sum_{j=1}^m C^{(j)} Q_{\text{obs}}^{(j)} \quad (3)$$

is a direct consequence of Equations 1 and 2 above. Because the quantities C_k^{obs} and $Q_{\text{obs}}^{(j)}$ are imperfectly observed values, Equation 3 almost certainly fails. Consequently, the system described by Equations 1 and 2 is expected to be mathematically inconsistent. Further complications stem from the nonnegativity of the variables $x_k^{(j)}$, as well as the restriction that their summations over k not exceed unity. We therefore consider each of the Equations 1 and 2 to be merely a goal.

Given a choice of values for the variables $x_k^{(j)}$, we measure our satisfaction with this choice in terms of nonnegative multiples of the squared residuals for each of these equations. Having specified (on some basis) a weight W to each of the $m+n$ equations (Eqs. 1 and 2 above), we define an optimal occupancy as one which minimizes the function

$$T = \sum_{j=1}^m W_Q^{(j)} \left(\sum_{k=1}^n x_k^{(j)} Q_k - Q_{\text{obs}}^{(j)} \right)^2 + \sum_{k=1}^n W_C^k \left(\sum_{j=1}^m x_k^{(j)} C^{(j)} - C_k^{\text{obs}} \right)^2 \quad (4)$$

over all $x_k^{(j)} \geq 0$, ($k = 1, \dots, n$; $j = 1, \dots, m$) subject to $\sum_{k=1}^n x_k^{(j)} \leq 1$, ($j = 1, \dots, m$). The value T in Equation 4 is dimensionless, because each weight W is taken in units given by the reciprocal of those for the corresponding equation. We also allow for infinite weights, meaning that the associated equation holds as an enforced constraint. The allowance for variable weights offers great flexibility in this method of estimating site occupancies, and we have thus allowed a selection of separate weights for each site and chemical substituent, as illustrated in examples below.

The mathematical optimization problems arising from the different possible combinations of nonnegative and infinite weights are examples of convex quadratic programming problems. As such, they have well-understood theoretical properties and there are several software packages available for their solution. We refer the reader to the texts of Fletcher (1980) and Lawson and Hanson (1974) for background. As a quick first attempt at solving one of the above problems, one can ignore the nonnegativity constraints and introduce Lagrange multipliers for the goals enforced as equations. The resulting optimality conditions consist of a system of linear equations that may be solved using ordinary Gaussian elimination. If a solution is found which is nonnegative, it is necessarily optimal. Otherwise, one will probably need to use some quadratic program solver.

TABLE 1. Notation used in determination of site occupancies

Type	Symbol	Description
Problem size	m	number of sites
	n	number of atomic species (cations)
Variables	$x_k^{(j)}$	occupancy fraction of species k in site j
Formal (integer) quantities	Z_k	formal valence of species k
	Q_k	scattering power (e.g., atomic number) of species k
	$C^{(j)}$	rank for site j , i.e., number of equivalent locations per unit cell
Chosen (integer) quantity	$c^{(j)}$	number of bonds to site j (neighborhood specified by user)
Observed values	$d_i^{(j)}$	mean bond distance from site j to the i th anion in its coordination polyhedron
	$Q_{\text{obs}}^{(j)}$	site scattering (e.g., electron count) at site j
	C_k^{obs}	analyzed amount of species k (atoms per unit cell)
Bond Valence Values	b	data-fitting parameter
	R_{ki}	bond distance for species k , bond i (when bond valence is one vu)
Bond Length Values	$V_k^{(j)}$	bond valence sum for species k at site j^*
	$\bar{d}^{(j)}$	observed average bond distance at site $j^\dagger$
	$\bar{d}_k^{(j)}$	average bond distance for species k at site $j^\ddagger$
Weights	$W_Q^{(j)}$	$\in [0, \infty]$: weight applied to goal in Equation 1 for site j
	W_C^k	$\in [0, \infty]$: weight applied to goal in Equation 2 for species k
	$W_Q^{(j)}$	$\in [0, \infty]$: weight applied to goal in Equation 5 for site j
	$W_D^{(j)}$	$\in [0, \infty]$: weight applied to goal in Equation 7 for site j

* Calculated as:

$$V_k^{(j)} = \sum_{i=1}^{c^{(j)}} \exp \left(\frac{R_{ki} - d_i^{(j)}}{b} \right).$$

† Calculated as:

$$\bar{d}^{(j)} = \frac{1}{c^{(j)}} \sum_{i=1}^{c^{(j)}} d_i^{(j)}.$$

‡ Calculated (from bond valence) as:

$$\bar{d}_k^{(j)} = -b \ln(Z_k / c^{(j)}) + \frac{1}{c^{(j)}} \sum_{i=1}^{c^{(j)}} R_{ki}.$$

The optimal occupancy is generally not unique for any choice of weights, as the set of optimal solutions forms a convex polytope in the space of all possible occupancies. Equations 1 and 2 describe a linear system with $m + n$ equations and mn variables. Roughly speaking, a unique assignment can be expected (when all weights are positive) for a problem with two sites and two species, whereas an assignment of four species to three sites leaves at least five extra degrees of freedom. An exact prior determination of the number of degrees of freedom is unlikely; the restriction of nonnegativity and the possibility of full occupancy typically remove further degrees of freedom. The theoretical and practical aspects of determining the uniqueness and robustness of optimal assignments are a matter of continuing research. Nevertheless, it is clear that additional side conditions must be added in order to determine the unique correct assignment. As mentioned earlier, traditional attempts rely on making various simplifying assumptions. We will present an alternative approach to this difficulty, which relies on the notion of “site valence.”

SITE VALENCE

Extending Pauling’s second rule, Brown (1981) defined the valence-sum rule in terms of a single cation occupying a site. Hawthorne et al. (1993) restated this rule for multiply occupied sites: “when averaged over the whole structure, the sum of the bond valences incident at a site is equal to the average atom valence at that site.” To formalize this extended rule, we define site valence as the weighted average valence of the n species possible at a multiply occupied site. We distinguish between the formal site valence $\sum_{k=1}^n x_k^{(j)} Z_k$ and the apparent site valence (O’Keeffe 1989) as $\sum_{k=1}^n x_k^{(j)} V_k^{(j)}$. Here Z_k and $V_k^{(j)}$ denote, respectively, the formal valence for species k and the bond-valence sum $V_k^{(j)}$ for species k at site j .

Using this nomenclature, the above statement of Hawthorne et al. can be formalized as

$$\sum_{k=1}^n x_k^{(j)} Z_k \equiv \sum_{k=1}^n x_k^{(j)} V_k^{(j)}, \text{ for each site } j. \quad (5)$$

Brown and Shannon (1973) used such a relation in an unsuccessful attempt to determine site occupancies in feldspars for only two substituents. Indeed, the presence of strain will prevent Relation 5 from holding as an equality even for perfectly observed data.

Nevertheless, we suggest that the corresponding weighted squared residual term

$$\sum_{j=1}^m W_V^{(j)} \left[\sum_{k=1}^n x_k^{(j)} (Z_k - V_k^{(j)}) \right]^2$$

be incorporated in the minimization objective in Equation 4 as another goal. With this modification, the method of optimizing occupancies now consists of minimizing

$$T^* = \sum_{j=1}^m W_Q^{(j)} \left(\sum_{k=1}^n x_k^{(j)} Q_k - Q_{\text{obs}}^{(j)} \right)^2 + \sum_{k=1}^n W_k^C \left(\sum_{j=1}^m x_k^{(j)} C^{(j)} - C_k^{\text{obs}} \right)^2 + \sum_{j=1}^m W_V^{(j)} \left[\sum_{k=1}^n x_k^{(j)} (Z_k - V_k^{(j)}) \right]^2 \quad (6)$$

over all $x_k^{(j)} \geq 0$, ($k = 1, \dots, n$; $j = 1, \dots, m$) subject to $\sum_{k=1}^n x_k^{(j)} \leq 1$, ($j = 1, \dots, m$). In the case where zero values are specified for the weights $W_V^{(j)}$, we recover the original objective function in Equation 4.

We include site valence in our formulation because we expect the correct occupancy will make the apparent site valence as close as possible to the formal site valence whenever the earlier Equations 1 and 2 can be strictly enforced. In crystals with no strain the relation (Eq. 5) becomes an equation for the correct representation of apparent valence. Furthermore, there is a tendency (in the mathematical sense) for the apparent valence to approach the formal valence in all crystals, regardless of strain.

It may sometimes be desirable to revise the formulation of the apparent valence $V_k^{(j)}$ so that Relation 5 is an equation for all crystals in a given family of structures. We currently use the bond-valence formulation of Brown and Altermatt (1985) and of Brese and O’Keeffe (1991), which involves parameters R and b . In our software implementation, we have provided default values taken from those two papers, but the user may supply other values as deemed necessary.

Because site valence is included as a goal instead of an enforced constraint, it effectively reduces the number of degrees of freedom without strictly enforcing any simplifying assumptions. The formulation using Equation 6 still corresponds to a linear system that might, in some cases, be underdetermined. Interestingly, our experience so far indicates that the variation among optimal assignments is actually very small, on the order of the error in the data measurements. Moreover, we have observed that, at optimality, many of the assigned occupancies are zero. In other words, the nonnegativity constraints are playing an active role in restricting the possible solutions, effectively eliminating even more degrees of freedom. Furthermore, those sites that are expected to be full usually are, even without imposing full occupancy. In this way, the method itself leads to “simplifications” of the sort often imposed as assumptions, but chooses these simplifications on a solid mathematical basis. From the point of view of the crystallographer, the (near) uniqueness of the optimal assignment provides new evidence for the absence of homometric structures.

The final feature that we allow in our model involves the close correlation between the sum of expected mean bond lengths $\sum_{k=1}^n x_k^{(j)} D_k^{(j)}$ (based on ionic radii) with the observed mean bond lengths $\sum_{k=1}^n x_k^{(j)} \hat{d}^{(j)}$ incident to each site j . This correlation is widely used as a check for the correctness of occupancy assignments. For convenience, the approximation

$$\sum_{k=1}^n x_k^{(j)} D_k^{(j)} \equiv \sum_{k=1}^n x_k^{(j)} \hat{d}^{(j)}, \text{ for each site } j, \quad (7)$$

may be monitored by adding the term

$$\sum_{j=1}^m W_D^{(j)} \left[\sum_{k=1}^n x_k^{(j)} (D_k^{(j)} - \hat{d}^{(j)}) \right]^2 \quad (8)$$

to the formula in Equation 6. Because of the close connection between the Relations 5 and 7, one expects that minimizing T^* in Equation 6 would give a small value for the expression in Formula 8; this has been confirmed by our experience. Never-

theless, the approximation in Relation 7 is sometimes inaccurate; consequently, we set each weight $W_D^{(j)}$ to a default value of zero and allow the user to view the residuals as site assignments are generated.

To allow widespread use, we have written OCCQP using the quadratic programming capabilities available in *MATLAB*, a widely used mathematical package available through The MathWorks, Inc., 24 Prime Park Way, Natick, MA 01760-1500, U.S.A. OCCQP has a graphical user-interface for convenient analysis and optimization of site occupancies. Use of this program is described here. The OCCQP program and user guide can be obtained at <http://www.minsocam.org>.

We consider three examples from the literature to demonstrate the utility of the method. The first example, a tourmaline, is a moderately complicated structure with well-characterized site occupancies; it demonstrates the concordance of our solutions with those of a prior, careful study. The second example, a spinel, is a simpler structure in which assumptions (based on Mössbauer spectroscopy) were made in the original assignment; our method resolves these assumptions and improves on the earlier analysis providing lower residuals for all goals. This example also illustrates the advantages of the quadratic programming approach over ordinary least squares. The third example, an amphibole, nicely illustrates the use of OCCQP in generating a good starting point that is easily refined to provide a correct assignment.

EXAMPLES

Tourmaline

In a reassessment of cation ordering in the tourmaline atomic arrangement, Hawthorne et al. (1993) presented a detailed analysis of ordering of cations occupying the Y and Z octahedral sites in a dravite. These authors provided positional parameters (hence bond lengths), quantitative chemical data, and site-scattering values for the sites. To test OCCQP, we re-examined their site assignments. Table 2 presents the user-input file for this dravite example. Input is minimal, and includes title, atom types to be modeled, unit-cell contents of each atom (in atoms/unit cell), desired site nomenclature, observed site-scattering, rank of each site, coordination number of each site, and the distance and anion type for each bond.

The initial solution obtained with the program OCCQP places a small amount of Na in the Y site (≤ 0.011 atoms/site), but we believe this assignment results from imperfectly observed data and that these ions are contained solely in the X site. We thus fix the Na and Ca occupancies of the Y and Z sites at zero; no other assumptions are made. We use the default weights of unity for the chemistry, site scattering and valence terms, and zero weights for all bond-length terms.

Figure 1a displays the interface with the results of the original assignments, and Figure 1b displays the solution after execution of our algorithm. Comparison of the published site assignments and the optimized assignments show that the

TABLE 2. Input data for optimization of site occupancies in Hawthorne et al. (1993) dravite tourmaline

```

Name = 'Hawthorne et al. (1993) Tourmaline: X,Y&Z sites';
% Atoms are input as below
Atoms ={'Al' 'Ti(IV)' 'Cr(III)' 'Fe(III)' 'Fe(II)' 'Mg' 'Mn(II)' 'Ca' 'Na' 'K' };
% COBS is atoms/unit cell of each occupant
Cobs =[ 6.075 0.030 0.006 0.560 0.051 2.211 0.003 0.009 0.814 0.014 ];
% Desire site nomenclature, in this case we use standard tourmaline nomenclature
Sites ={'X' 'Y' 'Z' };
% Electron occupancy of each site, from site scattering refinement
Qobs =[ 9.27 15.15 13.03 ];
% C = rank of each site
C = [ 1 3 6 ];
% Coord = coordination number of each site
Coord = [ 9 6 6 ];
% Bond distances and anion type are input; allowable anions include O, F, Cl, S
%      d anions
dA = { 2.504 'O' % begin site X
       2.504 'O'
       2.504 'O'
       2.817 'O'
       2.817 'O'
       2.817 'O'
       2.746 'O'
       2.746 'O'
       2.746 'O'
       1.953 'O' % begin site Y
       2.002 'O'
       2.002 'O'
       2.117 'O'
       1.989 'O'
       1.989 'O'
       2.002 'O' % begin site Z
       1.915 'O'
       1.960 'O'
       1.908 'O'
       1.931 'O'
       1.900 'O' };

```

Note: In *MATLAB* programming language, "%" denotes a "Comment".

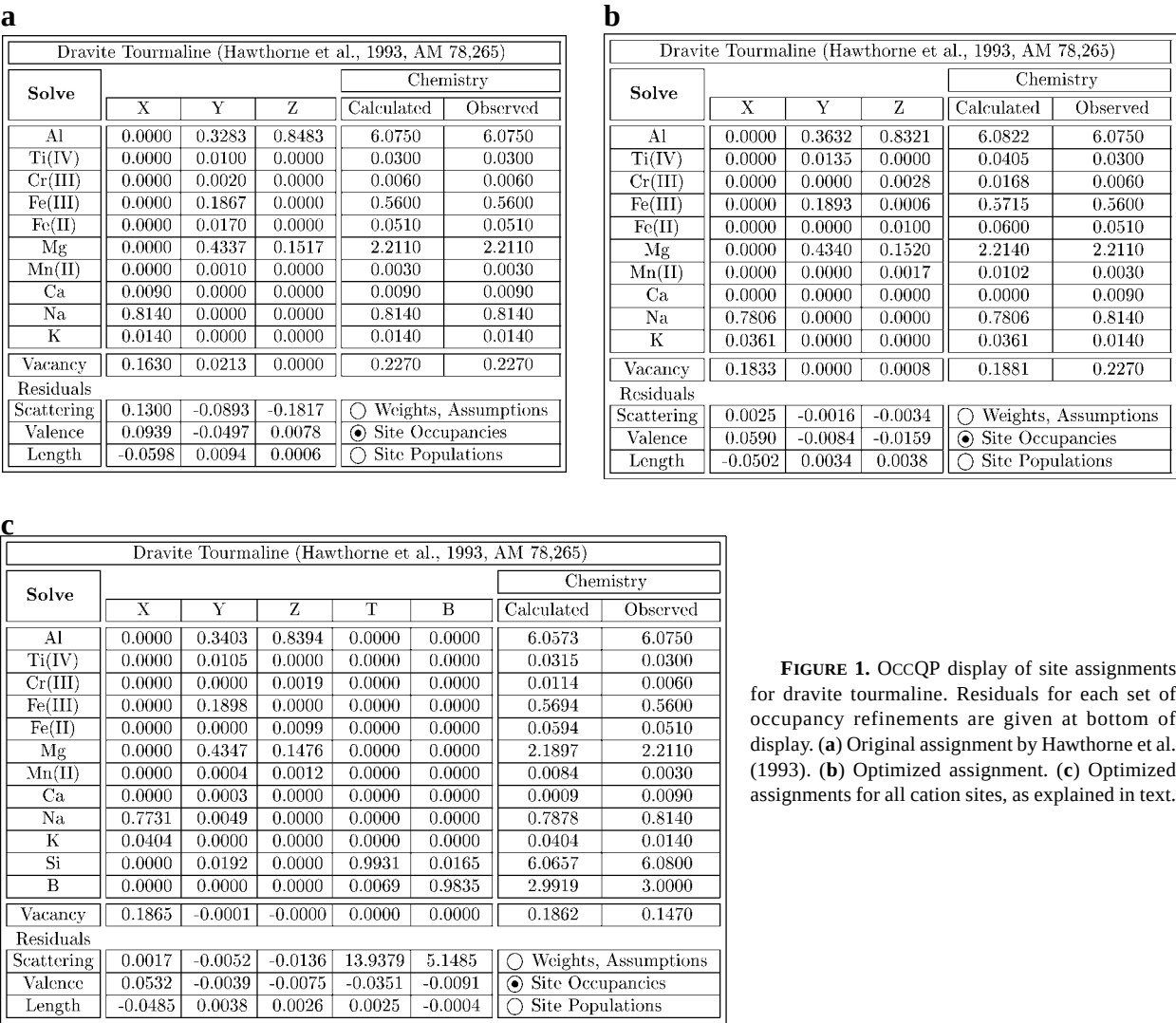


FIGURE 1. OCCQP display of site assignments for dravite tourmaline. Residuals for each set of occupancy refinements are given at bottom of display. **(a)** Original assignment by Hawthorne et al. (1993). **(b)** Optimized assignment. **(c)** Optimized assignments for all cation sites, as explained in text.

discrepancies are small, as much a testament to this method as to the careful site assignments of Hawthorne et al. (1993). Our method proposes slight differences in site assignments, but clearly the results must be weighed in terms of various crystal-chemical considerations. Note that the optimized solution correctly identifies the Y and Z sites as fully occupied, even though we do not constrain them as such.

As a challenge to the method, we attempted to predict all cation site occupancies in the structure, including the B and T sites, without the assumption of full occupancy. The input data were similar to those in Table 2, but also included the T and B sites. We use the default goals and weights: no site is constrained to be full, and unit weights are assigned to the site scattering, valence, and chemistry terms. We made exceptions for the B and T sites: Hawthorne et al. (1993) did not provide site-scattering values for those sites, so the corresponding terms were not refined (i.e., $W_Q^{(B)} = W_Q^{(T)} = 0$). (We assume that Hawthorne et al. (1993) did not refine the site scattering at all the cation sites because of the high correlation between site scattering and scale

factor when too many sites are released.) The program was thus charged with optimizing site occupancies of the T, B, X, Y, and Z sites, given only the analyzed chemistry, the electron occupancies of the X, Y, and Z sites, and bond lengths to each site. We use the default goals and weights: no site is constrained to be full, and unit weights are assigned to the site scattering, valence, and chemistry terms. The results displayed in Figure 1c constitute an excellent starting point for analysis of site occupancy.

Spinel

In a study of cation partitioning vs. temperature, Pavese et al. (1999) considered a synthetic spinel of composition $(Mg_{0.70}Fe_{0.23})Al_{1.97}O_4$. The site assignment involves up to four species (with Fe in either of two oxidation states) and two sites (tetrahedral and octahedral); the site scattering and chemical analysis Equations 1 and 2 therefore correspond to a linear system with eight unknowns and five equations. Pavese et al. (1999) proposed a least-squares formulation to solve this problem, namely by minimizing

$$T_p = \sum_{j=1}^m W_Q^{(j)} \left(\sum_{k=1}^n x_k^{(j)} Q_k - Q_{\text{obs}}^{(j)} \right)^2 + \sum_{k=0}^n W_k^C \left(\sum_{j=1}^m x_k^{(j)} C^{(j)} - C_k^{\text{obs}} \right)^2 + \sum_{j=1}^m W_D^{(j)} \left[\sum_{k=0}^n x_k^{(j)} \left(D^{(j)} - \hat{d}^{(j)} \right) \right]^2 + \sum_{j=1}^m W_O^{(j)} \left(1 - \sum_{k=0}^n x_k^{(j)} \right)^2 \quad (9)$$

over all $x_k^{(j)} \geq 0$, ($k = 0, \dots, n$; $j = 1, \dots, m$). This formulation has been couched in notation similar to that used in this paper to facilitate a comparison. Several remarks are needed for clarity. First, the Q term represents neutron site scattering in this example; OCCQP allows using neutron scattering length as an alternative to electron occupancy (the default), the latter being used in X-ray studies. Second, an explicit variable $x_0^{(j)}$ has been included to represent the vacancy at each site j . Third, the final term with weights $W_O^{(j)}$ amounts to replacing the occupancy restriction $\sum_{k=1}^n x_k^{(j)} \leq 1$ with a goal in the objective. In accordance with statistical data-fitting procedures, Pavese et al. (1999) recommend using weights given by the reciprocals of the variances of the corresponding measurements.

The model actually used by Pavese et al. (1999) in their calculations differs from the proposed formulation Equation 9 in several ways. First, because they anticipate difficulties with the bond-length term (as do we—see the caveats below), they replace it with a similar term involving the thermal expansion coefficients. This thermal expansion goal is algebraically equivalent to the bond-length goal, but has the advantage that reliable numbers exist for the given cations in octahedral coordination with oxygen. However, because such numbers are unavailable for tetrahedral coordination, they (effectively) set the weight corresponding to $W_D^{(j)}$ for that site to zero. Second, Pavese et al. (1999) restrict the number of degrees of freedom by strictly enforcing a simplifying assumption: they hold the assignment of Fe fixed during optimization. This assumption is based on their interpretation of Mössbauer spectroscopic data, indicating that all Fe resides in the tetrahedral site. In Figure 2a we display the site assignment proposed by Pavese et al. (1999), at the initial 300 K, with the corresponding residuals. Note that the bond-valence and bond-length residuals are fairly large; indeed, the bond valences would seem to indicate that this is a highly strained structure, contrary to the accepted view regarding spinels.

At the recommendation of one of the reviewers, we applied the OCCQP program to these data. We used the default settings corresponding to unit weights for site scattering, chemical analysis, and bond valence, with zero weights for bond lengths, no fixed occupancies, and variable vacancies at both sites. In particular, we make no assumptions regarding the assignment of Fe. The results are shown in Figure 2b. It is very gratifying to see that the optimization places the Fe entirely in the tetrahedral site, agreeing with, but independent of, the spectroscopic analysis. In addition, the residuals for site scattering, bond valence, and bond length are significantly better than those given by the published assignment, whereas the chemistry residuals are affected only slightly. On the other hand, the distribution of Al and Mg differs significantly from the assignment given by Pavese et al. Given a choice between the published and optimized results, we believe that most crystal chemists would prefer the latter as a point of departure for a serious analysis of site assignment in this spinel.

If thermal expansion were a valid proxy for bond length, one might expect Pavese et al. to have obtained results similar to ours. Why do the results differ so much? There are two readily apparent reasons. First, enforcing the occupancy equation

$$\sum_{k=0}^n x_k^{(j)} = 1$$

is a perfectly sound approach because it involves *no* observed data. Rewriting it as a soft goal, as in Pavese et al. (1999), is inappropriate, and introduces undue distortion in the objective function. Second, linear least squares problems and convex quadratic programs can be solved exactly in finite time using exact arithmetic; a floating-point version of such a method is used by OCCQP. In contrast, Pavese et al. use an iterative method based on MINUIT (James and Roos 1975) and a simulated annealing technique (Goffe et al. 1994). Using such a method for linear least squares is inappropriate, as it is intended for highly nonlinear least squares problems and does not take advantage of the special features of the linear case. Simulated annealing is a global optimization heuristic whose convergence properties are poorly understood. At the same time, MINUIT is a local optimization routine that must be terminated by hopeful, but less-than-rigorous, criteria. It is generally better to use appropriate software for the preferred formulation than to re-

a					b				
Spinel, 300K (Pavese et al. 1999, Phys.Chem.Min., 26, 242-250)					Spinel, 300K (Pavese et al. 1999, Phys.Chem.Min., 26, 242-250)				
Solve	Chemistry				Solve	Chemistry			
	T	M	Calculated	Observed		T	M	Calculated	Observed
Mg	0.5881	0.0558	0.6997	0.7000	Mg	0.4571	0.1318	0.7207	0.7000
Al	0.0819	0.9445	1.9709	1.9700	Al	0.2150	0.8621	1.9392	1.9700
Fe(III)	0.2300	0.0000	0.2300	0.2300	Fe(III)	0.2215	0.0061	0.2337	0.2300
Vacancy	0.1000	-0.0003	0.0994	0.1000	Vacancy	0.1064	0.0000	0.1064	0.1000
Residuals					Residuals				
Scattering	0.0228	-0.0122	○ Weights, Assumptions		Scattering	-0.0098	0.0061	○ Weights, Assumptions	
Valence	-0.1257	0.1851	● Site Occupancies		Valence	0.0395	0.0783	● Site Occupancies	
Length	0.0243	-0.0227	○ Site Populations		Length	-0.0009	-0.0075	○ Site Populations	

FIGURE 2. OCCQP display of site assignments for spinel of Pavese et al. (1999). Residuals for each set of occupancy refinements are given at bottom of display. (a) Original assignment by Pavese et al. (1999). (b) Optimized assignment.

formulate a model to overcome the shortcomings of a specific software package.

Amphibole

Our final example is an amphibole, ungarrettiite, recently analyzed by Hawthorne et al. (1995). This example illustrates the performance of our method on a structure exhibiting significant strain. The *M* sites form a closed component of this structure (as regards cation assignment), so we optimized only over those. Again we used the default goals: unit weights on chemistry, charge, and valence, with zero weight on bond lengths. No occupancies were fixed or excluded. Figures 3a and 3b show, respectively, the results of the published assignment and the optimized assignment. These are in good agreement, with the primary difference being that the optimization assigns a small quantity of Mn³⁺ to the M2 site, a possibility overruled (by fiat) in the analysis of Hawthorne et al. (1995). At the same time, all of the residuals for charge, valence and bond length are similar or better in the optimized solution. This example shows that the bond valence goal can assist in eliminating degrees of freedom without sacrificing the validity of the assignment made, even for strained structures. Again, the optimized solution immediately provides a very good first attempt at the assignment problem.

CAVEATS

We re-assert that our method provides a mathematically sound starting point for the careful crystallographer to assign site occupants; only this, and nothing more. The method formalizes the principles that structure analysts have utilized in numerous previous studies of mixed-occupancy sites. We urge crystallographers to use the method as a guide to determine site occupants, one that ensures rigor in conclusions about site occupancies. We note here several caveats that must be taken into account in utilization of the method. We emphasize that this discussion involves only X-ray (or neutron) structural and chemical data; the site assignment can be made even more successful by including other information such as spectroscopic analysis, as illustrated in the spinel example above.

First, the results of the optimization method are only as good as the input data. As we analyze earlier studies we find that oft-invoked assumptions yield unreasonable residuals; indeed, we

are finding that previously published studies are a fruitful source of data for re-examination of crystal-chemical principles (assumptions).

Second, this mathematically robust method must be tempered with crystal-chemical intuition, given that observations are not perfect. For example, in applications of the method we find examples of Si being placed in octahedral or trigonal sites in small amounts (on the order of 0.01 atoms/site). We believe such assignments result from imperfectly measured data, and have provided a method for excluding such assignments in the minimization. However, we suggest that if “unacceptable” assignments occur repeatedly, perhaps we must reassess our biases.

Third, a note is warranted about bond lengths. We note again that the default weight on the bond-length term is zero; this term is not included in the optimization (unless indicated by the user) because of known variations in average bond lengths for like polyhedra among different structure types. Average cation-anion interatomic distances are often calculated from atomic radii, the latter being available in numerous tables providing values for cations in specific coordination with oxygen or other anions. However, such tables often lack values for uncommon coordination, and thus are not universally applicable. In the program OCCQP we calculate ideal bond distances for any cation-anion pair on the basis of bond-valence constants. The average bond distance $D_k^{(j)}$ for species *k* at site *j*, with coordination number $c^{(j)}$, is then calculated as:

$$D_k^{(j)} = \frac{1}{c^{(j)}} \sum_{i=1}^{c^{(j)}} R_{ki} - b \ln(Z_k / c^{(j)})$$

This formulation allows calculation of an ideal bond distance for any ion in any coordination. Discrepancies between bond distances calculated using this method and those determined by summing radii are small, and reflect inaccuracies in the constants used in the first method or radii in the second.

Finally, a comment on weights must be made. Variable weights give the user the freedom to weight observations in proportion to their perceived accuracy or importance. Infinite weights should be used sparingly: an enforced equation amounts to a declaration of perfectly observed data. As noted in the discussion of Equation 3, using infinite weights on all chemistry and site-scattering goals invariably creates an inconsistent sys-

Ungarrettiite U2 (Hawthorne et al. 1995, Am. Min., 80, 165)						
Solve					Chemistry	
	M1	M2	M3	M4	Calculated	Observed
Mn(III)	0.9500	0.0000	0.9300	0.0000	2.8300	2.8300
Mn(II)	0.0500	0.8900	0.0000	0.0000	1.8800	1.8800
Mg	0.0000	0.1100	0.0700	0.0000	0.2900	0.2900
Ca	0.0000	0.0000	0.0000	0.0150	0.0300	0.0300
Na	0.0000	0.0000	0.0000	0.9850	1.9700	1.9700
Vacancy	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Residuals						
Scattering	-0.0700	-0.0300	-0.0100	-0.0850	○ Weights, Assumptions	
Valence	-0.0825	-0.1769	-0.1156	-0.0165	● Site Occupancies	
Length	-0.0029	0.0141	0.0116	-0.0447	○ Site Populations	

Ungarrettiite U2 (Hawthorne et al. 1995, Am. Min., 80, 165)						
Solve					Chemistry	
	M1	M2	M3	M4	Calculated	Observed
Mn(III)	0.9237	0.0462	0.9482	0.0000	2.8880	2.8300
Mn(II)	0.0763	0.8456	0.0000	0.0108	1.8654	1.8800
Mg	0.0000	0.1082	0.0328	0.0089	0.2670	0.2900
Ca	0.0000	0.0000	0.0000	0.0065	0.0130	0.0300
Na	0.0000	0.0000	0.0000	0.9738	1.9476	1.9700
Vacancy	0.0000	0.0000	0.0190	0.0000	0.0190	0.0000
Residuals						
Scattering	-0.0700	-0.0066	-0.0014	-0.0014	○ Weights, Assumptions	
Valence	-0.1155	-0.1236	-0.0958	0.0022	● Site Occupancies	
Length	0.0019	0.0060	0.0084	-0.0501	○ Site Populations	

FIGURE 3. OCCQP display of site assignments for ungarrettiite of Hawthorne et al. (1995). Residuals for each set of occupancy refinements are given at bottom of display. (a) Original assignment by Hawthorne et al. (1995). (b) Optimized assignment.

tem. Furthermore, using infinite weights on chemistry for prevalent species tends to create numerical errors (floating-point difficulties) that cause the program to stall, regardless of the underlying solver.

CONCLUSIONS

The research described herein began by treating the site assignment problem as a data-fitting problem. The problem is usually rank-deficient (i.e., underdetermined) when only the observed site scattering and chemical analysis are used. This difficulty is not unique to the present formulation, but is the site assignment problem. Least-squares models incorporating various assumptions have been used in earlier papers such as the formulation of Pavese et al. (1999) in the above spinel example. Instead of starting with a list of simplifying assumptions, we recommend minimizing the residual between formal and apparent valences, as this often solves the problem with a crystal-chemically acceptable solution. At times, the "simplifications" generated in solving the optimization problem force species out of certain sites, also solving the problem. At the very least, the assignment obtained by our method provides an excellent initial assignment of the site occupancies, and we believe OCCQP will prove to be very useful for the practicing crystallographer.

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