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# SITE POPULATIONS IN MINERALS: TERMINOLOGY AND PRESENTATION OF RESULTS OF CRYSTAL-STRUCTURE REFINEMENT

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## ABSTRACT

Definitions are proposed for the terms *site, structural formula, site occupancy, site-scattering value,* and *site population.* The results of site-scattering refinement should be presented in a chemically independent manner in terms of effective *epfu* (*e*lectrons *per f*ormula *u*nit) for X-ray structure-refinement and in terms of aggregate scattering-length for neutron structure-refinement. With the terminology proposed here, there is a direct correspondence between the refined site-scattering values, site populations, the structural formula and the formula unit of the mineral. Hopefully, this will make the results of structure refinement more clear to other branches of the Earth Sciences.

*Keywords:* structure refinement, site, site occupancy, site population, site-scattering value, structural formula, formula unit.

## SOMMAIRE

Nous proposons ici une définition des termes *site, formule structurale, occupation d'un site, valeur de la dispersion associée à un site,* et *population d'un site.* Il est souhaitable de présenter les résultats de l'affinement de la dispersion associée à un site de façon chimiquement indépendante en citant le nombre effectif d'électrons par unité formulaire dans le cas d'un affinement de la structure par diffraction X, ou la longueur cumulative de la dispersion dans le cas d'un affinement par diffraction neutronique. Avec les termes tels que définis ici, il se trouve a y avoir une correspondance directe parmi les valeurs affinées de la dispersion associée à un site, la population d'atomes sur un site, la formule structurale et l'unité formulaire d'un minéral. Nous espérons que ces définitions clarifieront les résultats d'affinements de structures pour les intéressés des autres branches des sciences de la terre.

(Traduit par la Rédaction)

*Mots-clés:* affinement d'une structure, site, occupation d'un site, population d'un site, valeur de la dispersion associée à un site, formule structurale, unité formulaire.

## INTRODUCTION

For the last few years, we have been applying crystal-structure refinement (SREF: Structure REFinement) of rock-forming minerals to problems in petrology. In the review process, it has become apparent that we need to be more careful and more consistent with our terminology concerning "site occupancies" or "site populations" in minerals. Reviewers who are not crystallographers express two principal concerns: (1) What is the difference (if any) between the terms "site occupancy" and "site population"? (2) If a "site-occupancy" refinement gives the "occupancies" of a site in terms of one set of atoms (*e.g.*, Mg and Fe, or Na and Ca), how can one then assign other atoms (*e.g.*, Al and Ti, or K) to that site?

These points may be considered trivial by crystallographers, but they are hindering the accessibility of SREF results to petrologists and geochemists, the very people who wish to use them. Here, we propose a set of definitions intended to obviate these problems and convey SREF results to the petrologist or geochemist in as straightforward a manner as possible. Below, we define and discuss terminology and use the *C*2/*m* amphibole structure as an example; we emphasize that we are referring to the characteristics of a structure as averaged over many unit cells (long-range characteristics).

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## TERMINOLOGY

Terminology used here is defined formally in Table 1; each definition is further amplified in the sections below.

### *Site*

The term *site* denotes any point occupied, or potentially occupied, by an atom within the unit cell of a structure; this definition allows vacancies to occur at a site in a structure (*e.g.*, as at the $A$ site in amphiboles). Sites are identified by letter symbols [*e.g.*, $M(1)$, $T(2)$, $Y$, O(3)]. In isostructural minerals, corresponding sites carry the same label, even though their atomic coordinates may vary somewhat from one structure to another; they are defined with reference to their structural environment. In minerals, different chemical species are commonly distributed among symmetrically equivalent sites in a crystal. Thus in amphiboles, the aggregate $M(1)$ site is commonly occupied by Mg and $Fe^{2+}$. Diffraction techniques give a description of a site (in terms of total scattering and relative position within the unit cell) that is the weighted mean of symmetrically equivalent sites in the crystal.

### *Structural formula*

A *structural formula* is the minimum set of symmetrically distinct sites that constitute the structural arrangement. As examples, consider the *C2/m* amphibole and *Pbca* orthopyroxene structures:

*C2/m* amphibole: $A\ M(4)_2\ [M(1)_2M(2)_2M(3)]\ [T(1)_4T(2)_4]\ O_{22}\ O(3)_2$

*Pbca* orthopyroxene: $[M1\ M2]\ [\mathrm{Si}A\ \mathrm{Si}B]\ O_6$

By convention (and for convenience), all anion sites occupied solely by $O^{2-}$ are summed and expressed as $O_n$. The structural formula corresponds closely to the *general formula*:

*C2/m* amphibole: $A\ B_2\ C_5\ T_8\ O_{22}\ W_2$

*Pbca* orthopyroxene: $X\ Y\ T_2\ O_6$

where

$A =$ Na, K, □ (vacancy), Ca $\equiv A$
$B =$ Ca, Na, $Fe^{2+}$, $Mn^{2+}$, Mg $\equiv M(4)$
$C =$ Mg, $Fe^{2+}$, $Mn^{2+}$, Al, $Fe^{3+}$, $Ti^{4+}$, Li $\equiv M(1), M(2), M(3)$
$T =$ Si, Al, $Ti^{4+}$ $\equiv T(1), T(2)$
$W =$ OH, F, Cl, $O^{2-}$ $\equiv$ O(3)

and

$X =$ Mg, $Fe^{2+}$ $\equiv M2$
$Y =$ Mg, $Fe^{2+}$, Al $\equiv M1$
$T =$ Si, Al $\equiv$ Si$A$, Si$B$

Note that the *general formula* does not always correspond to the *formula unit* as conventionally defined. Thus the general formula of enstatite is $Mg_2Si_2O_6$, whereas the formula unit is usually written as $MgSiO_3$. The latter formulation obscures the fact that the orthopyroxene structure contains two crystallographically distinct sites that are both occupied by Mg in end-member enstatite, but which do not accept $Fe^{2+}$ to the same extent in enstatite–ferrosilite solid-solutions. In this regard, we recommend that the formula unit be defined as corresponding to the structural formula.

TABLE 1. TERMINOLOGY FOR THE RESULTS OF CRYSTAL-STRUCTURE REFINEMENT

| | |
|---|---|
| SITE: | Any point within the unit cell occupied, or potentially occupied, by an atom. |
| STRUCTURAL FORMULA: | The minimum set of symmetrically distinct *sites* that, in conjunction with the symmetry operators of the crystal, constitute the crystal-structure arrangement. |
| SITE OCCUPANCY: | The total atomic content assigned to a site and normalized to unity. |
| SITE-SCATTERING VALUE: | The total scattering from a specific set of symmetrically equivalent sites in the structural formula. |
| SITE POPULATION: | The chemical species assigned to a set of symmetrically equivalent sites in a structural formula. |

### *Site-scattering refinement*

In the refinement of a crystal structure with more than one type of atom (scattering species) occupying a site, we actually determine the *total scattering-power* at that site. We do *not* uniquely determine the chemical species at that site from the structure refinement alone. We can interpret the refined total-scattering-power at a site in terms of chemical species *only* if we incorporate additional information into the interpretation procedure. Thus we can interpret the total scattering power at the $M(1)$ site in glaucophane in terms of chemical species *only* if we specify (1) which chemical species are involved (Mg, $Fe^{2+}$), and if (2) no vacancies occur at that site. Note that we can use the wrong scattering species in the refinement procedure, but will get (approximately) the correct amount of total scattering. For this reason, we propose to refer to this procedure as *site-scattering refinement.*

When expressing the results of a site-scattering refinement, two important factors must be considered: (1) The results should be expressed in an objective manner; thus we should not give the results in terms of the chemical species used in the refinement (*e.g.*, Mg and Fe, or Na), as *a posteriori* we could well re-assign this scattering to other species (*e.g.*, Al and Ti, or K and □). (2) The results should be conformable with the structural formula of the mineral; this might seem a trivial point, but for complicated minerals such as amphibole or staurolite, this practice greatly simplifies the relation between crystal structure and chemical composition.

### *Chemically independent representation of the results of site-scattering refinement*

Point (1) may be satisfied in the following manner for both X-ray and neutron crystal-structure refinement.

*X-ray scattering:* X rays are scattered by electrons, and we can express the total amount of scattering from a site in terms of *the number of electrons associated with the atoms at that site.* As the number of electrons in an atom is equal to its atomic number (see Appendix 1, particularly with reference to valence state), it is easy to convert effective scattering at a site (in electrons) to chemical species, and *vice versa.* Thus the refined scattering from the site can be converted to a chemically independent representation of the site-scattering refinement, the *mean atomic number* (*MAN*). For some crystal-chemical purposes, this is a very useful quantity, particularly in the assignment of complex site-populations involving several different chemical species.

*Neutron scattering:* We can express the total amount of neutron scattering from a site directly in terms of the aggregate scattering-length. This may then be further interpreted with the incorporation of additional chemical information.

### *Site-scattering value*

Point (2) may be satisfied by defining the *site-scattering value* as the *total scattering from the symmetrically equivalent sites in the structural formula, expressed in epfu* (electrons *per formula unit*). Thus for X rays, the magnitude of the site-scattering value is equal to the MAN multiplied by the multiplicity *N* of the site in the structural formula. We propose that the site-scattering values be given as chemically independent results of site-scattering refinement.

### *Site occupancy*

In the refinement of a crystal structure, the total scattering from a site (*S*) is often described, *via* the use of linear constraints, by the equation

$$S = x\,f_1 + (1-x)\,f_2 \qquad (1)$$

where $x$ can be a fixed (usually 1.0) or a variable ($0 \leq x \leq 1$) parameter, and $f_i$ are the scattering powers of the species (atoms or vacancy) at that site in the structure. The parameters $x$ and $(1-x)$ are the occupancies of that site, and must be associated with the specific atom species denoted as 1 and 2. This equation may readily be generalized for occupancy of a site by more than two scattering species:

$$S = \Sigma^{n}_{i=1}\, x_i\, f_i \text{ where } \Sigma x_i = 1 \qquad (2)$$

However, as only $S$ is determined by the refinement procedure, $x_i$ are actually indeterminate, and equation (2) has a unique solution only if we *externally* specify the values of $x_i$ (i = 1, n–2) (*i.e.*, assume values perhaps from results of a chemical analysis of the crystal).

We propose that the term *occupancy* be used *where the total contents of a site are normalized to unity* (*i.e.*, use of *some* structure-refinement software, use in thermodynamic formulations). The word "*occupy*" may be used in referring to the fact that an atom occurs at a specific site: thus Mg and $Fe^{2+}$ occupy the *M*(1) site in most amphibole crystals.

### *Site population*

*Site population* is defined as the chemical species assigned to the symmetrically equivalent sites in the structural formula, and is expressed in *a*toms *p*er *f*ormula *u*nit (apfu) for the results of both X-ray and neutron crystal-structure refinement. The advantages of this definition of site population are clear. On the one hand, the site-scattering value is the effective scattering of that site population. On the other hand, where we deal with a mineral formula that is the direct chemical equivalent of the structural formula, the site populations sum *directly* to give the structural formula. This one-to-one correspondence avoids confusion, particularly for very complicated minerals with partly occupied sites (*e.g.*, amphibole, staurolite).

The site population proposed for a particular site *must* be consistent with the requirements of the refined site-scattering value, mean bond-length and local bond-valence requirements; the complete crystal-chemical formula must obey the requirement that the formal valences of all atoms in the crystal sum to zero.

### *An example: glaucophane*

Table 2 shows the results of a (hypothetical) site-scattering refinement for glaucophane of composition $K_{0.08}$ $(Na_{1.84}Ca_{0.16})$ $(Mg_{2.57}Fe^{2+}_{0.61}Al_{1.62}Fe^{3+}_{0.20})$ $(Si_{7.94}Al_{0.06})$ $O_{22}$ $(OH)_2$. The site-scattering values

TABLE 2. SITES, SITE-SCATTERING VALUES AND SITE POPULATIONS IN A HYPOTHETICAL GLAUCOPHANE CRYSTAL

| Site | MAN | N | Site scattering (epfu) | Site populations (apfu) |
|---|---|---|---|---|
| *M*(1) | 14.10 | 2 | 28.20 | 1.70 Mg + 0.30 $Fe^{2+}$ |
| *M*(2) | 14.21 | 2 | 28.42 | 0.18 Mg + 1.62 Al + 0.20 $Fe^{3+}$ |
| *M*(3) | 16.34 | 1 | 16.34 | 0.69 Mg + 0.31 $Fe^{2+}$ |
| *M*(4) | 11.72 | 2 | 23.44 | 1.84 Na + 0.16 Ca |
| *A* | 1.52 | 1 | 1.52 | 0.08 K + 1.92 □ (vacancy) |

N = number of equivalent sites in the structural formula correspond directly to the site populations; thus for $M(1)$, 1.70 × 12 (Mg) + 0.30 × 26 (Fe) = 28.2 epfu. Note that the assignment of specific site-populations requires information in addition to the refined site-scattering values; it requires some knowledge of the composition of the amphibole (not necessarily an exact composition) *and* consideration of local stereochemistry. Site populations were assigned on the basis of: (1) observed site-scattering values; (2) observed mean bond-lengths; (3) absence of vacancies at any of the $M$ sites (these are forbidden by local bond-valence requirements); (4) overall electroneutrality (the requirement that the formal valences of all atoms in the crystal sum to zero). Thus all trivalent cations were assigned to $M(2)$.

## SUMMARY

We propose that crystallographers quote site-scattering values as a chemically independent expression of the results of their structure refinement, together with any site populations that they subsequently assign. A one-to-one correspondence among site-scattering values, site populations, structural formula and formula unit will make the whole process much more straightforward and transparent to crystallographers and non-crystallographers alike.

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## APPENDIX 1.

## DETAILS CONCERNING X-RAY REFINEMENT PROCEDURES AND THE CALCULATION OF MAN FOR OXIDE AND OXYSALT MINERALS

Extensive methodological tests at the CSCC (Pavia) during the refinement of ~1500 rock-forming minerals [*e.g.*, garnet (Merli *et al.* 1995), pyroxene (Rossi & Ungaretti 1989), amphibole (Ungaretti 1980, Ungaretti *et al.* 1983), mica (Oberti *et al.* 1993a), titanite (Oberti *et al.* 1991), staurolite (Hawthorne *et al.* 1993), epidote] have shown that the most accurate results are obtained by (1) using ionized X-ray scattering curves for non-tetrahedral cations, and (2) refining the occupancy of ionized *versus* neutral species for anions ($O^{2-}$ *versus* O) and tetrahedral cations ($Si^{4+}_{x}Al^{3+}_{1-x}$ *versus* $Si_xAl_{1-x}$). In general, formal charges ranging between +1 and +2 are obtained for Si, indicating the strong covalent character of the Si–O bond. In most of the refined minerals, the first residual in the difference-Fourier map occurs midway along the *T*–O bonds, and corresponds to the electron density involved in the Si–O bond.

Ionization state affects only very few reflections (those with $0 \leq \sin\theta/\lambda \leq 0.25$, *i.e.*, a very low percentage of the reflections collected in a standard X-ray experiment up to $\theta = 30$–$35°$ with Mo radiation; for amphiboles, the intensities of 15 out of ~1400 independent reflections (up to $\theta = 30°$) are affected in the range 2–5% by ionization state, and the intensities of a further 30 reflections are slightly (<2%) affected. The X-ray scattering curves of Fe, $Fe^{2+}$ and $Fe^{3+}$ are identical beyond $\sin\theta/\lambda = 0.25$ (Fig. 1), showing that the atomic number is representative of the X-ray scattering of all the valence states. Therefore, the MAN must always be calculated with reference to the atomic numbers of the scattering species. This also means that different oxidation states cannot be distinguished directly by site-scattering refinement. Complete site-populations, including valence states, may be determined from the refined site-scattering values and site geometry in those cases where the ionic radii of polyvalent elements are significantly different (*e.g.*, $^{[6]}Fe^{2+}$ = 0.780, $^{[6]}Fe^{3+}$ = 0.645 Å; Shannon 1976).

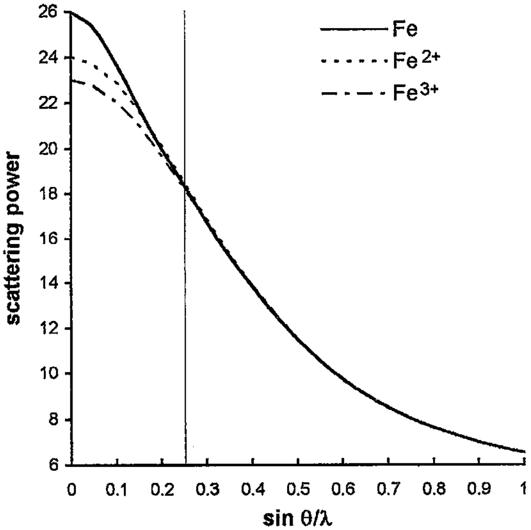

FIG. 1. The shape of the X-ray scattering-curves for different oxidation states of Fe as a function of $\sin\theta/\lambda$.

The scattering power is a function of $\sin\theta/\lambda$ and of the atomic number of the scattering species. Thus the scattering power for $Mg^{2+}$ does not differ from that of $Al^{3+}$ at $\sin\theta/\lambda = 0$, but differs by (3.288 – 3.851) = –0.586 electrons (*i.e.*, 17%) at $\sin\theta/\lambda = 0.70$ (corresponding to $\theta = 30°$ for Mo*K*α radiation). For this reason, accurate results are only obtained where the correct scattering curves are used. An incorrect choice of the chemical species present at a particular site (*i.e.*, of the X-ray scattering factors used in the site-scattering refinement) may produce small changes in MAN (≤2%) and larger changes in the displacement factor [see Ungaretti (1980) and Oberti *et al.* (1992, 1993b) for examples of the *M*(2), *T*(2) and *O*(3) sites in amphiboles].