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.

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.