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CRYSTAL-STRUCTURE ANALYSIS AS A CHEMICAL ANALYTICAL METHOD: APPLICATION TO LIGHT ELEMENTS

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ABSTRACT

Crystal-structure analysis is an electron-counting technique with spatial resolution. As such, it directly determines the chemical formula of a mineral, and should be considered as an acceptable method of chemical analysis for crystals. It is particularly effective for first- and second-row elements, most of which cannot be detected by all except the most modern electron microprobes. It needs only the smallest amount of sample (albeit a single crystal), and consumes no material whatsoever in the analytical process. As such, it is an ideal method for the chemical characterization of new minerals. Here we document its use to derive the correct formulae of a series of minerals involving all the light elements (of the first and second rows of the periodic table); for most of these minerals, conventional methods of analysis had given the wrong amount of the light element(s) present, or had failed to detect such elements altogether. The success of crystal-structure methods in determining the correct chemistry of these minerals shows crystal-structure analysis to be a *bona fide* method of chemical analysis.

Keywords: crystal-structure analysis, chemical analysis, light elements.

SOMMAIRE

L'ébauche d'une structure cristalline est en fait un comptage des électrons et une détermination de leur résolution spatiale. Ainsi, elle permet de déterminer la formule chimique d'un minéral, et devrait donc être considérée à juste titre comme méthode d'analyse des cristaux. Elle est particulièrement efficace pour les éléments des première et deuxième rangées, dont la plupart ne peuvent être décelées, sauf en utilisant une microsonde électronique très perfectionnée. La méthode ne requiert qu'une quantité infime de matériau, qui doit cependant être monocristallin, et n'est aucunement destructrice. Elle est donc idéale pour la caractérisation des espèces minérales nouvelles. Nous l'illustrons pour dériver la formule correcte d'une série de minéraux porteurs de tous les éléments légers des première et deuxième rangées de la table périodique. Dans la plupart des cas, les méthodes conventionnelles d'analyse avaient indiqué des proportions erronées des éléments légers présents, ou bien ne les avaient tout simplement pas signalés. Les succès de la méthode préconisée en font un véritable moyen de déterminer la composition chimique d'une structure cristalline.

(Traduit par la Rédaction)

Mots-clés: analyse d'une structure cristalline, analyse chimique, éléments légers.

INTRODUCTION

Mineralogy has its most fundamental basis in chemistry. Most mineralogists intuitively believe that they do not "know" a mineral until they know its chemical formula. Once we know the chemical formula, we believe that we have a firm hold on what the mineral actually is, and that all other measurements merely extend our knowledge of its chemical and physical properties and its geological occurrence. Consequently, the characterization of the chemical formula of a mineral is of considerable significance in mineralogy. Analytical methods are dominated by the electron microprobe; combined energy-dispersion spectrometry (EDS) and wavelength-dispersion spectrometry (WDS) are extremely powerful. The former can identify the elements present, which is of particular importance in detecting (mineralogically) unusual components in minerals; the latter can provide accurate analyses at the microscopic level. The drawbacks of electron-microprobe analysis are well known: (i) it cannot distinguish between valence states; (ii) it cannot analyze for all of the light elements. By and large, (i) is the more serious deficiency, as the valence state of Fe is of great importance in the chemistry of many common rock-forming minerals. However, (ii) assumes considerable importance in the characterization of new minerals. Many new minerals occur in highly fractionated environments enriched in the "incompatible" elements, important among which are the first- and second-row elements. Modern electron microprobes are sensitive to some of these elements, but many mineralogists do not have access to such equipment. The same argument applies to the ion microprobe; this can now give reliable analyses for some first- and second-row elements, but is not generally accessible.

There are many methods of chemical analysis that are available to us (*e.g.*, Potts 1987, Jeffery & Hutchinson 1981). However, many of these are not suitable for mineral analysis because of one crucial fact: they require more sample material than often is available. This problem is particularly acute in the characterization of new minerals, for which there is often only a minute amount of material. In extreme cases, this restriction can even apply to the electron microprobe; with only one small single crystal available, one does not wish to grind half of it away preparing a polished section for analysis. Another problem is associated with the methods that consume material; one does not wish to analyze for a specific element just to check whether or not it is present, as this could use up a lot of material just to produce a series of null results. Of course, EDS electron-microprobe analysis is a powerful technique in this regard, and thus more or less restricts this problem to light elements.

The results from standard techniques of chemical analysis are usually presented as a series of oxides (expressed in wt.%) from which a mineral formula is calculated *via* some scheme of normalization that usually relates to the crystal structure of the mineral; in addition, the amount of oxygen is always assumed, rather than measured. Crystal-structure analysis provides a much more direct measurement of the formula of a mineral. It is essentially an electron-counting technique with spatial resolution. As such, it can identify the different elements on the basis of their different X-ray scattering powers, and their spatial distribution in the (averaged) unit cell of the crystal. In addition to this direct information, we also get additional data on the stereochemical details of the crystal, details that can often resolve questions concerning valence states of transition metals, or the amount (and role) of hydrogen in the mineral. The use of crystal-structure analysis in this regard has gradually increased as the accuracy of the experimental methods has improved. Thus Warren (1929) used Pauling's second rule to show that amphiboles have two hydrogen atoms per formula unit, present as hydroxyl groups. In the 1960s, attempts to derive patterns of ordering in rock-forming silicates by unconstrained site-occupancy refinement were often unsuccessful owing to the presence of systematic error in the intensity data. However, improvements in techniques and instrumentation over the past 20 years have virtually eliminated this problem, and unconstrained refinement generally gives reliable chemical compositions. There is still some reluctance to accept crystal-structure analysis as a technique of chemical analysis, despite the fact that it is more direct than most conventional analytical methods, as it gives the chemical formula directly. In this paper, we document the use of crystal-structure analysis to derive the correct formula of a series of minerals involving all compound-forming elements of the first and second rows of the periodic table.

DETERMINATION OF A CHEMICAL FORMULA

The discussion will be organized by element; first the conventional techniques for the analysis of the element will be briefly outlined, with an indication of the amount of material required for the analytical procedures where appropriate, together with some of the drawbacks of the current methods. The intention here is not to denigrate the utility of these methods, but to draw attention to the fact that there are problems, and that these can, to a significant extent, be handled by crystal-structure analysis. Following this, an example of a recent structural determination of this element in a mineral is discussed and, where appropriate, the resulting structure is examined with bond-valence theory (Brown 1981) to check on the validity of the results.

Hydrogen

Hydrogen can be quite difficult to analyze for using standard techniques; the usual wet-chemical methods require considerable amounts of sample

(~ 1 g). This situation can be greatly improved using a hydrogen extraction line, but the amount of material required (~ 50 mg) still can be a problem. In addition, it is difficult to distinguish between adsorbed H_2O and H_2O evolved from low-temperature dehydration reactions in both of these methods. Ion-microprobe techniques have greatly improved in the last few years, and quantitative analysis is now feasible (Hervig 1988, Hervig *et al.* 1987, Jones & Smith 1984); however, this method is still not widely available. In addition, the high-vacuum requirements can induce low-temperature dehydration reactions in many hydrates.

Mandarinoite is a hydrated ferric iron selenite first described by Dunn *et al.* (1978) from the Pacajake mine, Colquechaca, Bolivia, and later reported from the De Lamar silver mine, Owyhee County, Idaho. An electron-microprobe analysis showed the presence of Fe and Se, and the formula $Fe^{3+}{}_2Se_3O_9{\cdot}4H_2O$ was assigned. The H_2O was not determined directly owing to the paucity of material, but was assumed to be the difference between the sum of Fe_2O_3 and SeO_2 (obtained by electron-microprobe analysis) and 100%. If the reported formula is used to calculate the mean index of refraction *via* the Gladstone–Dale relationship, the agreement is not very good, and the compatibility index (Mandarino 1981) is poor. The good agreement in optical properties between mandarinoite from Bolivia and Idaho (Lasmanis *et al.* 1981, Table 1) suggests that the formula assigned to mandarinoite was not correct.

The structure of mandarinoite was solved by Hawthorne (1984). It consists of a very open heteropolyhedral framework of $[Fe^{3+}O_4(H_2O)_2]$ and $[Fe^{3+}O_5(H_2O)]$ octahedra and (SeO_3) triangular pyramids; the cavities within this framework are filled with an ordered array of hydrogen-bonded (H_2O) groups. The formula indicated by the structural analysis is $Fe^{3+}{}_2Se_3O_9{\cdot}6H_2O$ rather than the $Fe^{3+}{}_2Se_3O_9{\cdot}4H_2O$ proposed in the previous study. Comparison of the composition derived by electron-microprobe analysis with the composition derived from the structural formula is shown in Table 1; the microprobe Fe_2O_3 and SeO_2 values are ~ 6 % too high. There are six independent (H_2O) groups in the mandarinoite structure, only three of which are bonded to the principal cations. The remaining (H_2O) groups occur in the zeolite-like cavities of the $(FeO_6)(SeO_3)$ framework, and are held in the structure by hydrogen bonding. These observations suggest that mandarinoite may have lost H_2O during electron-microprobe analysis, a danger if a mineral contains significant zeolitic H_2O.

Lithium

Li is a common element in highly fractionated environments, in which it can be a significant component in major phases (*e.g.*, spodumene, amblygonite–montebrasite, tourmaline, lepidolite). It also can occur in some more common silicate minerals that scavenge Li in less-fractionated environments (*e.g.*, staurolite, riebeckite). Li cannot be detected by the electron microprobe, but can be quantitatively analyzed for by the ion microprobe (Dutrow *et al.* 1986). Li can also be determined both by flame spectrophotometry and by atomic absorption spectrometry; in both cases, the amount of sample required is ~ 100 mg.

TABLE 1. CHEMICAL COMPOSITION OF MANDARINOITE

	Microprobe	Structure
Fe_2O_3	28.68 wt.%	26.86 wt.%
SeO_2	59.53	55.98
H_2O	(11.79)	17.16
Sum	100.00	100.00

The crystal structure of a fluor-riebeckite from Pikes Peak, Colorado, was refined by Hawthorne (1978). The chemical analysis showed that there is no significant Mg in the amphibole, and thus the scattering from the *C*-group sites was expected to be totally dominated by Fe. Unconstrained site-occupancy refinement showed the scattering at the *M*(3) site to be significantly less than the scattering at the *M*(1) and *M*(2) sites; in terms of the number of electrons, the refined site-occupancies were 26, 25 and 18.5 e, respectively. Normally, one would presume that Mg was ordered at the *M*(3) site, but the chemical analysis showed insignificant Mg. From the analyzed amount of Fe, it was apparent that the substituent cation (scattering species) at *M*(3) must have a very low atomic number. Of the early first-row elements, only Li is compatible with octahedral coordination by oxygen, and Li is also an expected element in the paragenesis of this particular amphibole. Consequently, Fe and Li were assigned to both the *M*(1) and *M*(3) sites, and the Li occupancy was refined for these two positions; convergence of the refinement showed Li to be completely ordered at the *M*(3) site.

The amphibole was then analyzed for Li by atomic absorption spectrometry; recalculation of the formula unit showed the Li to belong to the *C*-group cations, and the amount was found to be in close agreement with the Li value derived from the refinement. The refinement was repeated with the analyzed Li content as a constraint on the site-occupancy refinement, but the results were essentially the same as the unconstrained values. Such site-occupancy refinement will in general be an extremely sensitive indicator of the amount of Li present, as Li has a much lower scattering power than most of the cations for which it substitutes.

TABLE 2. EMPIRICAL BOND-VALENCE TABLE FOR EHRLEITE

	P(1)	P(2)	P(3)	Be	Zn	Ca(1)	Ca(2)	W(1)	W(1)	W(2)	W(2)	W(3)	W(3)	W(4)	W(4)	H(10)	Sum
O(1)	1.310					0.198 0.300	0.243										2.051
O(2)	1.166				0.527		0.212		0.145								2.050
O(3)	1.185			0.535		0.228											1.948
O(4)	1.314			0.483						0.233							2.030
O(5)		1.299				0.248 0.295					(0.233)						2.075
O(6)		1.242		0.510		0.201											1.962
O(7)		1.303			0.498		0.310										2.111
O(8)		1.239		0.523				0.145									1.907
O(9)			1.253		0.501											0.215	1.969
O(10)			1.057												0.158	0.785	2.000
O(11)			1.423				0.339						0.157	0.158			2.077
O(12)			1.352		0.516							0.157					2.025
W(1)						0.289		0.855	0.855								1.999
W(2)						0.249	0.216			0.767	0.767						1.999
W(3)							0.315					0.843	0.843				2.001
W(4)							0.316							0.842	0.842		2.000
Sum	4.925	5.083	5.085	2.051	2.042	2.008	1.951	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

Beryllium

Beryllium is a fairly common element, particularly in fractionated granitic pegmatites. Even the most recent models of electron microprobe are not sensitive to Be, and one must generally rely on atomic absorption spectrometry. The ion microprobe is sensitive to Be, but there can be problems with accuracy (as in the example of ehrleite given below), probably arising from inadequate standardization. In addition, ion microprobes are not yet widely available, and obtaining access to one can be a problem. Atomic absorption spectrometry is quite a reliable method for Be, but it is still not a microanalytical method: ~ 100 mg of sample is necessary (Jeffery & Hutchinson 1981), and the amount of available material often precludes use of this technique.

Ehrleite is a hydrated zinco-beryllo-phosphate mineral described by Robinson *et al.* (1985) from the Tip Top pegmatite, South Dakota. Beryllium was analyzed for by ion microprobe, and H_2O was calculated by difference; although the ion microprobe confirmed the presence of hydrogen, the amount could not (then) be quantified. The ideal formula was given as $Ca_4Be_3Zn_2(PO_4)_6 \cdot 9H_2O$, but the measured contents of Be and H_2O (3.32 and 9.28 apfu-atoms per formula unit) were slightly in excess of the proposed ideal amounts. Ehrleite is triclinic, a fact that suggests some problems with the proposed formula, specifically the Be and H_2O contents. If the space group of ehrleite is $P\bar{1}$, at least one Be and one H_2O group must each occur at a special position on an inversion center. However, both (BeO_4) and (H_2O) are intrinsically noncentrosymmetric, and hence cannot occur (without gross positional disorder) at special positions in $P\bar{1}$. On the other hand, the amounts of all electron-microprobe-derived components of the mineral (Ca, Zn, P) are compatible with $P\bar{1}$ symmetry. This suggests that both Be and H_2O contents were incorrectly determined in the initial study.

The structure of ehrleite was solved in the space group $P\bar{1}$ by Hawthorne & Grice (1987). The dominant structural unit is a sheet of corner-sharing tetrahedra, linked by [7]- and [8]-coordinated Ca atoms and an extensive network of hydrogen bonds. The differences in scattering power at the various tetrahedrally coordinated sites easily distinguished between Be (Z = 4), P (Z = 15) and Zn (Z = 30); this identification was further supported by the observed mean bond-lengths at the three sites. In particular, the $<$Be–O$>$ distance of 1.624 Å is characteristic of complete occupancy of this tetrahedron by Be. This is confirmed by the bond-valence table (Table 2). The bond-valence sum around the Be position, calculated using the universal curves of Brown (1981), is 2.051 v.u., indicating that the formal charge at this position is +2. In addition, the bond-valence sums around the four coordinating anions [O(9), O(10), O(11) and O(12)] are close to their ideal values of 2.0 v.u., indicating that the magnitudes of the Be–O bond valences are correct. Four of the anions located in the structure solution [*W*(1), *W*(2),

$W(3)$ and $W(4)$] had bond-valence sums of 0.15 to 0.25 v.u.; in order for the bond-valence requirements around these anions to be satisfied, they each have to be bonded to two hydrogen atoms, which unequivocally identifies them as (H_2O). The resulting structural formula is $Ca_2Zn_{1-x}BeH_{2x}(PO_4)_2(PO_3OH)\cdot(H_2O)_4$, with $x = 0.10$ for $Z = 2$.

Boron

Boron is a much more common constituent of minerals than is generally realized. It is now detectible by the more recent models of electron microprobe, but not as part of their normal mode of operation; operating conditions have to be specifically set up for boron determination, with the resulting tendency for an operator not to look for boron unless it is expected. Boron may also be determined spectrophotometrically or titrimetrically. However, these methods normally require sample weights in excess of 100 mg, which generally precludes them for mineral analysis.

Poudretteite is a new member of the milarite group of minerals (Hawthorne & Smith 1986) recently discovered at Mont Saint-Hilaire, Quebec (Grice *et al.* 1987). This is a particularly interesting group of minerals from a stereochemical viewpoint. The basic structure is a framework of corner-sharing tetrahedra with channels extending along the Z axis, channels that are filled by an ordered arrangement of univalent and divalent cations. A prominent cluster in the framework is the $[T_{12}O_{30}]$ group, a double hexagonal ring of tetrahedra that are usually occupied by Si (but may be partly occupied by Al in some species). These clusters are cross-linked (into a framework) by a single tetrahedron. It is this single tetrahedron that makes this structure type of great interest. This tetrahedron may be occupied by a very wide range of cations (Li, Be, B, Mg, Al, Si, Fe^{3+}, Fe^{2+}, Mn^{2+}, Zn, Sn^{4+}, Zr), which gives the milarite-group minerals a very wide range of stability and occurrence.

The cell dimensions and space group indicated that poudretteite is a milarite-group mineral, but the cell dimensions are significantly different from known members of the milarite group, suggesting that it is a new member of the group. As the structure refinement progressed, it became apparent that a novel chemistry was involved. The general formula of the milarite-group minerals can be written as $A^{[6]}{}_2B^{[9]}{}_2C^{[12]}D^{[18]}T(2)^{[4]}{}_3T(1)^{[4]}{}_{12}O_{30}$. In the preliminary stages of refinement, both site scattering power and interatomic distances indicated the A, C and $T(1)$ sites to be occupied by Na, K and Si, respectively. At this stage, the mean interatomic distance at the $T(2)$ site was 1.47 Å, typical of B in tetrahedral coordination. Inclusion of B at $T(2)$ resulted in final convergence of the refinement at an R index of 3.3%. In the final cycles of refinement, the site occupancy of B at the $T(2)$ position was refined, and converged to a value of 0.94(2); this indicates that the $T(2)$ site is fully occupied by B (within the 3σ limits of experimental precision). Table 3 shows the bond-valence table for poudretteite. The bond-valence sum around the $T(2)$ position is 3.05 v.u., in agreement with the result of the site-occupancy refinement that this site is occupied by B^{3+}. This result is further supported by the fact that the bond-valence sums for oxygen are all close to their ideal values of 2.0 v.u. Complete occupancy of the $T(2)$ site by B corresponds to 11.2 wt.% B_2O_3, as calculated from the ideal formula $KNa_2B_3Si_{12}O_{30}$. Subsequent to the structure work, electron-microprobe analysis for boron gave 11.4 wt.%, in close agreement with the value derived from the structure refinement. This indicates that even with very light elements such as boron, site-occupancy refinement can give reliable results.

TABLE 3. EMPIRICAL BOND-VALENCE TABLE FOR POUDRETTEITE

	$^1Na^A$	K^C	$B^{T(2)}$	$Si^{T(1)}$	Sum
O(1)				$1.027^{\times 2}_{\rightarrow}$	2.054
O(2)		$0.081^{\times 12}_{\downarrow}$		1.024 1.003	2.108
O(3)	$0.194^{\times 6}_{\downarrow}$		$0.763^{\times 4}_{\downarrow}$	1.080	2.037
Sum	1.164	0.972	3.050	4.134	

[1] superscripts denote the site in the general milarite structure type

Carbon

Of interest to us here is carbon present as carbonate; other forms such as elemental carbon or organic matter are usually not relevant to mineral analysis, although carbides, oxalates, tartrates, *etc.*, may be important in very specific environments (meteorites, fulgurites, urinary calculi, wine bottles). Carbon can now be detected with modern electron microprobes. Although this must be done in a special mode of operation, the presence of carbonate in a mineral can commonly be inferred from its optical and physical properties, and hence the mineral can be specifically checked for C. However, for many minerals with mixed oxyanions [*e.g.*, (SiO_4) and (CO_3), or (PO_4) and (CO_3)], the presence of carbonate is not so easy to infer from physical properties, and the carbonate can be missed. There are many wet-chemical and gravimetric methods for the determination of carbon, but the methods based on high-temperature decomposition are of most general importance. Traditionally this has always required a considerable amount of sample, but more recent microanalytical methods have reduced this by an order of magnitude.

Sclarite is a hydroxyl-bearing zinc carbonate mineral recently found at the Franklin mine, New Jersey (Grice & Dunn 1989). An electron-microprobe analysis indicated the presence of Zn, Mg, Mn, and minor Fe; no oxyanionic component was detected. However, the diffraction pattern suggested that sclarite is isostructural with loseyite, $Mn_4Zn_2(Zn,Mg)(CO_3)(OH)_{10}$, and this was confirmed by crystal-structure analysis. The single carbonate group in the structure was readily identified by the nearly ideal triangular coordination of the C atom and the short C–O bonds. The bond-valence analysis is shown in Table 4. The bond-valence sum around the C position is 3.988 v.u., close to the ideal formal valence of carbon in a carbonate group. Five of the eight anion positions have bond-valence sums of 1.0 to 1.2 v.u., indicating that they are (OH) groups some of which participate (as donor anions) in significant hydrogen bonding. The remaining three anions have bond-valence sums of 1.8 v.u., indicating that they are O^{2-} anions that participate (as acceptor anions) in significant hydrogen bonding. The resulting formula is $(Zn,Mg,Mn)_4Zn_3(CO_3)_2(OH)_{10}$, with Zn in both tetrahedral and octahedral coordination, the site-occupancy refinements indicating that Mg substitutes for Zn at the octahedrally coordinated sites.

TABLE 4. EMPIRICAL BOND-VALENCE TABLE FOR SCLARITE

	Zn(1)	Zn(2)	Zn(3)	Zn(4)	C	Sum
O(1)			0.428		1.377	1.805
O(2)	0.292 0.369		0.477			1.138
O(3)	0.350	0.355	0.475			1.180
O(4)	0.347	0.281	0.501			1.129
O(5)		0.381		$0.607^{\times 2}\downarrow$		0.988
O(6)				$0.511^{\times 2}\downarrow$	1.330	1.841
O(7)	0.248	0.192			1.281	1.721
O(8)	0.335	0.348 0.363				1.046
Sum	1.941	1.920	1.881	2.236	3.988	

TABLE 5. EMPIRICAL BOND-VALENCE TABLE FOR UNGEMACHITE

	S	N	K	Na(1)	Na(2)	Fe^{3+}	H(5)A	H(5)B	Sum
O(1)	1.352			$0.158^{\times 3}\downarrow$		$0.524^{\times 6}\downarrow$			2.034
O(2)	1.584		$0.094^{\times 2}\downarrow$ $0.104^{\times 2}\downarrow$		0.209				1.991
O(3)	1.548		$0.126^{\times 2}\downarrow$		0.174			0.20	2.048
O(4)	1.566		$0.082^{\times 2}\downarrow$		0.189		0.20		2.037
O(5)				$0.212^{\times 3}\downarrow$	0.201		0.80	0.80	2.013
O(6)		$1.718^{\times 3}\downarrow$	$0.072^{\times 2}\downarrow$		0.143 0.144				2.077
Sum	6.050	5.154	0.956	1.110	1.060	3.140	1.00	1.00	

Nitrogen

Nitrogen is not a common element in minerals, and in normal circumstances, most minerals are not analyzed for it. It can be detected with modern electron microprobes, both by windowless or thin-window EDS methods and by low-current WDS; however, neither of these techniques is the normal mode of operation of a microprobe, and consequently the presence of nitrogen is very easy to miss. Various wet-chemical techniques for the determination of nitrogen are summarized by Jeffery & Hutchinson (1981). Of special note is the method described by Wlotzka (1961), which distinguishes between nitrogen present as ammonia and that present as nitrate.

Ungemachite is a complex hydrated sulfate mineral discovered by Bandy (1938) in his classic work on the northern Chilean sulfate deposits; it was formally described by Peacock & Bandy (1938). They assigned the formula $K_3Na_8Fe^{3+}(SO_4)_6(OH)_2 \cdot 10H_2O$, with $Z = 3$ and point symmetry $\bar{3}$. The structure of ungemachite was reported by Groat & Hawthorne (1986). As solution of the structure progressed, it became apparent that the formula originally assigned to ungemachite was somewhat incorrect. The $[K_3Na_8Fe^{3+}(SO_4)_6]$ part of the formula was located, together with an additional thirteen atoms, in contrast to the twelve ($O + H_2O$) anions indicated by the previously accepted formula. Of particular significance was an atom occupying the 6*c* position and surrounded by a triangle of other atoms ~ 1.25 Å away from the central atom. Both the difference-Fourier peak heights and the observed stereochemistry suggested a first- or second-row atom in triangular coordination by oxygen atoms. At this stage, a bond-valence calculation (Table 5) allowed identification of all anions as O^{2-}, OH^-, and $H_2O°$, and confirmed the proposed trivalent state of Fe in the structure. For the cell content to be electrostatically neutral, the additional atom had to be pentavalent. In addition, the observed mean bond-length of 1.25 Å for triangular coordination by oxygen is in good agreement with both the sum of the constituent ionic radii (–0.10 + 1.36 = 1.26 Å; Shannon 1976) and observed $\langle N^{[3]}–O \rangle$ distances in minerals and synthetic inorganic compounds. Refinement of this model converged to an *R* index of 3.9%, indicating excellent agreement between the structure model and the diffraction data.

The sum of the bond-valences around the N^{5+} site came to 5.15 v.u., in good agreement with the formal valence of nitrogen of 5+. In addition, the bond-valence requirements of the O(6) anions are satisfied, confirming that the N–O bond valence is correct. The resulting formula of ungemachite is $K_3Na_8Fe^{3+}(SO_4)_6(NO_3)_2 \cdot 6(H_2O)$; comparison with the original formula shows how the omission of essential oxyanion groups with cations of high formal charge can easily be compensated with regard to charge balance by an error in the OH/H_2O ratio.

Oxygen

Normally one does not analyze for oxygen. Rather it is assumed that a mineral contains the requisite amount of oxygen necessary to achieve electroneutrality in a structure containing the analytically determined cations and simple anions (*e.g.*, F, Cl, *etc.*). Errors in the amount of oxygen can arise in three different ways: (i) Cations are "missed" or incorrectly measured during analysis; for example, in ehrleite (see above), the errors in Be and H resulted in incorrect amounts of oxygen being assigned to the formula. (ii) Anions are missed or incorrectly measured; for example, in morinite (see below), the errors in F resulted in incorrect amounts of oxygen being assigned to the formula. (iii) There are errors in the assignment of valence states. Oxygen can be determined by the more modern electron microprobes, but this is not normally done in mineral analyses. There are various nuclear reaction methods for the analysis of oxygen, but these are rarely if ever used for minerals, and we rely on stoichiometry arguments and assumptions for oxygen "determination".

Schneiderhöhnite is an iron arsenite mineral first described by Ottemann *et al.* (1973) from Tsumeb, Namibia. The formula was given as $Fe^{2+}{}_8As^{3+}{}_{10}O_{23}$, and assumes the most reduced state for all cations in an oxygen-rich environment. The structure was solved by Hawthorne (1985), who showed that it has a very complicated and compact framework, with five distinct arsenite groups and four distinct Fe sites, all of which are in octahedral coordination. Thirteen unique oxygen atoms were located by difference-Fourier synthesis during the structure-solution process. None of these lie on special positions, which indicates that the oxygen stoichiometry is different from that proposed in the original description. The observed mean bond-lengths at the octahedrally coordinated cation sites are 2.011, 2.012, 2.035, 2.047, and 2.172 Å, respectively. The first four distances are compatible with complete occupancy by Fe^{3+} (r = 0.645 Å) and the fifth distance is compatible with occupancy by Fe^{2+} (r = 0.78 Å). The coordination of the arsenic atoms is triangular pyramidal, with mean bond-lengths of 1.785 ± 0.009 Å, compatible with As^{3+}. These valence assignments are in accord with the number of oxygen atoms found in the structure solution, leading to the formula $Fe^{2+}Fe^{3+}{}_3As^{3+}{}_5O_{13}$ (*i.e.*, $Fe_8As_{10}O_{26}$) rather than the $Fe^{2+}{}_8As^{3+}{}_{10}O_{23}$ originally assigned. Thus, in the determination of oxygen by structure refinement, not only do we determine oxygen directly, but we also have a check on the measured value *via* the electroneutrality principle.

Another example shows that the proportion of oxygen can be quantitatively determined by this technique, even in the presence of very heavy elements. Magnolite was originally described by Genth (1877) as a "mercurous telluarate" of probable formula Hg_2TeO_4. Owing to the small amount of material available, the species could not be described adequately, and remained a doubtful species for over a century. The principal difficulties associated with determining the correct chemistry of magnolite involve the analysis of the species O and H. Both heavy cations have two possible valence states: Hg^{1+} and Hg^{2+}, Te^{4+} and Te^{6+}; thus many possible formulae can be conceived. The crystal structure of magnolite was solved and refined by Grice (1989). Despite its large absorption coefficient (μ = 724 cm^{-1} for Mo$K\alpha$ radiation), the structure refined to an R index of 4.5%. Four atomic positions were located, and the scattering power at each site identified these as Hg, Te, O and O in a ratio 2:1:2:1. The resulting formula is Hg_2TeO_3. The electroneutrality principle gives only one possible solution for the valence states of Hg and Te: 1^+ and 4^+, respectively. Thus, the oxygen content and the cation valence states were successfully determined solely from the structure solution and refinement.

Fluorine

Fluorine commonly substitutes extensively for hydroxyl in many common rock-forming minerals, in addition to its occurrence in fluoride minerals *sensu stricto*. It can be analyzed for using modern electron microprobes in their normal WDS mode of

TABLE 6. EMPIRICAL BOND-VALENCE TABLE FOR MORINITE

	Ca	Al	Na	P(1)	P(2)	†H(1)	H(2)	H(3)	Sum
O(1)	$0.212\,{}^{\times2}\rightarrow$			1.292		0.26			1.980
O(2)		$0.577\,{}^{\times2}\rightarrow$				0.78			1.950
O(3)	$0.250\,{}^{\times2}\rightarrow$		0.192		1.246				1.938
O(4)			0.201		1.344			$0.25\,{}^{\times2}\rightarrow$	2.045
O(5)	$0.285\,{}^{\times2}\rightarrow$		0.167	1.270					2.007
O(6)	0.192	0.411					0.74	0.71	2.053
O(7)		0.553			$1.253\,{}^{\times2}\downarrow$		0.24		2.046
O(8)	0.212	0.524		$1.189\,{}^{\times2}\downarrow$					1.925
F(1)	0.274 0.330	0.466							1.070
	*(0.330) (0.391)	(0.596)							(1.317)
F(2)	0.281	0.523	$0.231\,{}^{\times2}\downarrow$						1.035
	*(0.338)	(0.668)	$(0.295\,{}^{\times2}\downarrow)$						(1.301)
Sum	2.036 (2.210)	3.054 (3.329)	1.022 (1.150)	4.940	5.096	1.04	0.98	0.96	

*values in parentheses are calculated using cation-oxygen curves for cation-fluorine bonds;
†hydrogen bond valences estimated such that the bond-valence sums around both anions and cations approach their ideal values.

operation, and comparison of electron-microprobe values with wet-chemical and optically derived values (*e.g.*, Groat *et al.* 1990) indicates that the former method is reliable. Fluorine can be determined by many different wet-chemical techniques. The most common current method uses an ion-selective electrode. The amount of sample required varies, depending on the amount of F present, but is normally of the order of 100–500 mg, which often precludes its use for new or zoned minerals.

Morinite is a hydrated aluminum fluor-phosphate found in granitic pegmatites. Fisher (1960) proposed the formula $Ca_4Na_2Al_4(PO_4)_4(OH_xF_{5-x})_2{\bullet}(5-x)H_2O$ with $x \sim 1.5$. The structure was solved by Hawthorne (1979), who essentially confirmed the formula proposed by Fisher, with slight modifications to the anionic part of the formula. As originally written, the formula suggests some sort of solid solution between (OH) and F, with the amount of H_2O varying accordingly. In the structure solution, least-squares refinement of an isotropic displacement model with all anions assigned as oxygen converged to an *R* index of 4.9%. At this stage, the isotropic displacement (*B*) factors for two of the anions were ~ 0.0 Å^2, as compared with 0.7 to 1.0 Å^2 for the other anions. A bond-valence calculation done at this stage (Table 6) using the curves of Brown & Wu (1976) showed sums around the two anions (with zero displacement factors) of ~ 1.3 v.u., indicating that the anions are monovalent; recalculation using bond-valence curves for cation–F bonds gave bond-valence sums around these anions of close to 1.0 v.u. (Table 6). Both the low isotropic displacement factors and the bond-valence calculations suggest that these two anions are F rather than (OH). Appropriate modification of the scattering curves at these two sites, followed by least-squares refinement, resulted in isotropic displacement factors comparable to the other anions, confirming the assignment of these anions as F. The resulting formula of morinite is $Ca_2NaAl_2F_4(OH)(H_2O)_2(PO_4)_2$, with an anion content (ignoring the phosphate ligands) of $F_4(OH)(H_2O)_2$ as compared with the previously assigned value of $F_{3.5}(OH)_{1.5}(H_2O)_{1.75}$. Because of the similarity in scattering powers of F and O, this method may not be very sensitive in dealing with OH–F solid solutions. However, where there is an ordered arrangement of OH, O, and F, as is the case for morinite, the method can work quite well.

TABLE 7. EMPIRICAL BOND-VALENCE TABLE FOR MOYDITE

	Y	B	C	H	Sum
O(1)	0.274 0.395		1.294		1.96
O(2)	0.423 0.297		1.303		2.02
O(3)	0.524		1.482		2.01
O(4)	0.303	0.784		1	2.09
O(5)	0.263	0.708		1	1.97
O(6)	0.270	0.689		1	1.96
O(7)	0.325	0.741		1	2.07
Sum	3.070	2.920	4.080		

AN IDEAL EXAMPLE: MOYDITE

Moydite is a mineral found at the Evans–Lou mine, a former feldspar–quartz producer that exploits a granitic pegmatite near Wakefield, Quebec. It was found in 1980, but the description was not published until 6 years later (Grice *et al.* 1986) because of significant analytical difficulties that arose during its original characterization. As is often the case with new minerals, there was only a minute quantity of the mineral available, which limited the choice of possible chemical techniques to microanalytical methods.

An electron-microprobe analysis showed the presence of significant Y and *REE* only. The structure was solved by Grice & Ercit (1986), the structure solution giving the chemical composition of the mineral. The position of a single heavy atom (Y,*REE*) was derived by direct methods, and the remaining atoms were found by difference-Fourier synthesis. Initially, all atoms (except Y,*REE*) were assigned the scattering factors of oxygen, and the model refined to an *R* index of 16%. At this stage, it was necessary to assign the correct scattering species to the various sites; this was done using local site-geometry. Two of the atoms are surrounded by several others at very short distances, indicating that these two atoms are cations rather than anions. Specifically, one atom is coordinated by three others in a triangular arrangement, with a mean separation of ~ 1.28 Å; this geometry suggests a carbonate group. The other atom is coordinated by four others in a tetrahedral arrangement, with a mean separation of ~ 1.48 Å; this geometry suggests a borate group. Suitable modification of the relevant site scattering-factors, together with least-squares refinement, led to convergence at an *R* index of 6% for an isotropic displacement model, confirming the assigned site-occupancies. Further refinement and difference-Fourier synthesis revealed no additional atoms. However, a bond-valence calculation (Table 7) showed the sums around the borate ligands to be ~ 1.0 v.u., indicating that they are hydroxyl rather than oxygen anions. The resulting formula of moydite is thus (Y,*REE*)$[B(OH)_4](CO_3)$.

Completion of the formal description of moydite was delayed for several years by the perceived need to characterize the chemistry by conventional analytical methods. First, a sample was examined by

Secondary-Ion Mass Spectrometry (SIMS). The SIMS analysis showed the presence of H, B, C, and O in addition to Y and the *REE*, but the quantitative results of the work were very misleading. The B:C ratio was determined as 12:1 using gaudefroyite, $Ca_4Mn_{3-x}(BO_3)_3(CO_3)(O,OH)_3$, as a standard, and as 3:1 with canavasite, $Mg_2(CO_3)(HBO_3){\cdot}5H_2O$, as a standard. The C:Y ratio was determined to be 2.5:1 with a synthetic yttrium carbonate standard. It became evident that the matrix corrections for these light elements were not adequate (at least at the time that these analyses were done), and that our standards were not sufficiently close in composition to the sample for accurate analysis. The laser microprobe mass analyzer (LAMMA) supported the elemental identifications of SIMS, but did not provide further quantitative information on the anion content. Moydite was also examined by laser Raman microprobe in an effort to directly identify the light oxyanion groups. The presence of a CO_3 group was confirmed, and an acid borate group (*i.e.*, bonded to H) was identified, but we could not tell if the borate group is triangular or tetrahedral. Subsequent to all of this work, we obtained access to a new electron microprobe equipped for the detection of light lithophile elements, and after some effort, accurate analyses were obtained. However, the quantitative results were found to be very sensitive to the standards used and to the details of the data-reduction procedures. Indeed, we judged the correctness of the electron-microprobe results according to the agreement they showed with the results of the crystal-structure determination.

CONCLUSIONS

We have documented the use of crystal-structure analysis to derive the correct formula of a series of minerals involving all the elements (except neon) of the first and second rows of the periodic table. For most of these minerals, conventional methods had given the wrong amounts of the light elements present, or had failed to detect them altogether. The success in determining the correct chemistry of these minerals effectively demonstrates that crystal-structure analysis is a *bona fide* method of chemical analysis.

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