

(sketches by Wendell Wilson)

from UNKNOWN to KNOWN



The characterization of new mineral species

by
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INTRODUCTION

The characterization of a new mineral species is an exciting, challenging, frustrating, arduous, and delightfully satisfying task. This paper was prepared at the request of the editor of the *Mineralogical Record* to acquaint the mineral collector and amateur mineralogist with procedures which should be followed to accurately and responsibly characterize a new mineral species. New mineral species are not rare; in fact they are quite abundant in major collections everywhere. Although the discovery of new species readily available to the average collector might seem to be proceeding slowly, there are in fact a large number of possible new minerals submitted to the IMA (International Mineralogical Association) Commission on New Minerals and Mineral Names each year. For example, there were 63 submitted in 1974, 37 in 1975, and 58 in 1976. The number of new species a scientist may discover and characterize is, at the present time, limited only by the number of "unknowns" he or she can acquire to work on, a certain amount of luck, and the amount of time and energy available to apply to their characterization. A rigorous discipline is required, for short-cuts can be extremely hazardous, and the intensive initial process consists of attempting to prove the unknown to be a known species. Hence, only by failing to identify an unknown can a new mineral be discovered.

THE UNKNOWN MINERAL

In the beginning...there must come together an unknown mineral and a mineralogist, the latter having the experience and knowledge necessary to unravel the mysteries of the former. Some new minerals are found by geologists, either in the field

during the investigation of an ore deposit, or as part of a detailed laboratory examination of a particular paragenesis. A large number of unknowns come to the professional mineralogist through mineral collectors of all persuasions and inclinations. Of particularly strong interest to the scientist are unknowns from very knowledgeable and astute collectors who have already done some preliminary work and given some thought to the available chemistry before sending the mineral to a mineralogist.

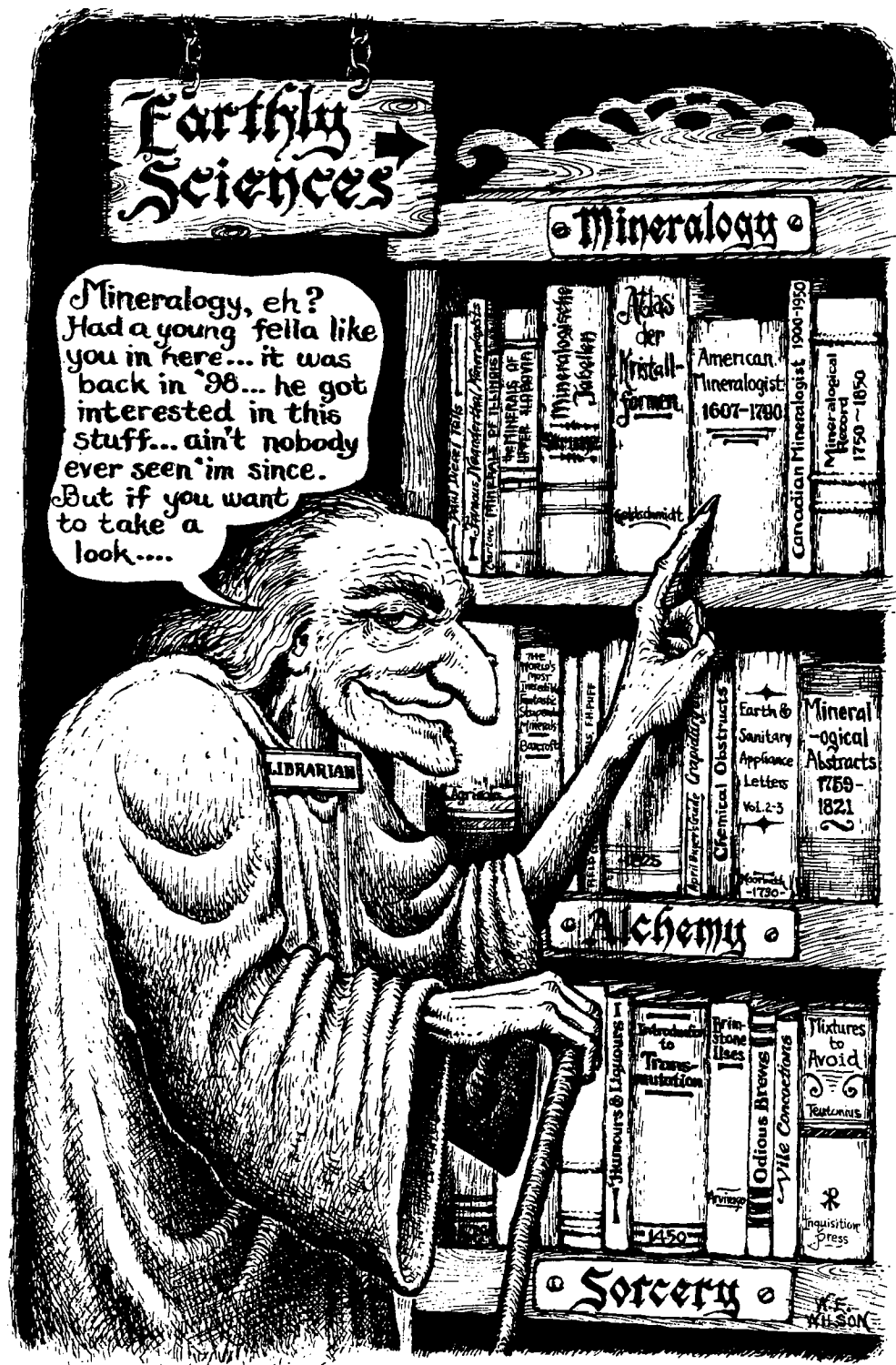
The mineral collector is a vital part of the process and his contributions are increasingly recognized. For advice on what to do with an unknown, the reader is referred to the guest editorial entitled "So You Think You Have A New Mineral?" (Dunn, 1975).

The role of the mineral dealer cannot be ignored because many new minerals have been recognized after having stimulated the interest of a dealer who was familiar with a particular deposit, and who took the effort to bring the mineral to a laboratory where it could be investigated.

Museum mineral collections provide many of the new species and the resident museum mineralogist has several advantages: the "unknowns" drawer is never empty, public inquiries are plentiful (astute ones less so), and the resources of the collection allow rapid and accurate comparisons. The museum collections also aid the mineralogist in the search for natural analogs of known species, establishing other relationships between a new mineral and similar species, and in providing additional samples from the locality of the unknown.

PHASE I - INITIAL ATTEMPTS

The initial attempt at identifying the unknown mineral is by



First
the mineralogist must
go to the library
and search the
literature.

eye, a careful observation of color, shape, luster, symmetry, cleavage and associated minerals will frequently suggest some possibilities and these are immediately checked before proceeding. The next step might be consultation with another mineralogist since experience is invaluable and a colleague may have seen similar material at some time in the past. Having thus far failed to identify the unknown, a perusal of other specimens of the associated species from the same locality or a similar paragenesis may suggest some possibilities which did not spring to mind initially. This initial attempt should be accompanied by a detailed writing down of one's observations. Since an active mineralogist may be pursuing 6-10 unknowns simultaneously (some being new species almost completely characterized), one should not rely too much on a mortal memory. While considering mortality, the taking of extensive notes also ensures

that one's work may be used by another scientist in case of death. Hence, the sum of one's observations is always available.

Most important is the chemistry of the host rock and associated minerals, if any. One should always investigate all the possibilities suggested by the "comfortable chemistry" viewpoint; *chemically similar minerals frequently occur together*. Hence, in a calcium silicate deposit, one expects, and finds, many calcium silicate minerals. If the matrix or host mineral for a colorful unknown is a badly altered tennantite $[(\text{Cu},\text{Fe})_{12}\text{As}_4\text{S}_{13}]$, which is assumed to have undergone supergene oxidation, one would pay particular attention to secondary copper and iron arsenates, sulfates, arsenate-sulfates, and oxides. The elements in the associated minerals should also be considered as they may mix during alteration. The dominant chemistry of the deposit may suggest some possibilities. An initial foray into the literature is now in order.

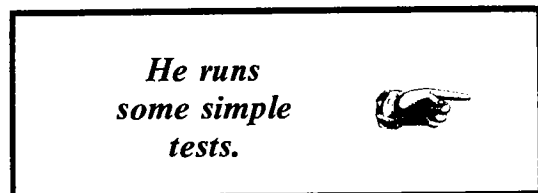
and available texts and reference works should be examined by looking up the minerals associated with the unknown and noting their "associates". Guidebooks to localities and detailed studies of the particular locality are sometimes available and may be most useful. Any leads are checked out as they develop by comparison of all diagnostic features and properties.

At this point, a reasonable argument can be advanced for putting the unknown and notes aside for a few days, and then returning to the accumulated data with a fresh viewpoint. By doing so, one might note features or relationships not noted during the initial observation. However, enthusiasm for the mineral is usually high and one might move immediately to Phase II.

PHASE II - THE ADVANCED METHODS

Having thus defied identification by the methods outlined above, the unknown is now worthy of a position on the roster of "things to be thoroughly investigated". The length of time the unknown awaits its turn for investigation may depend on a position determined by chronology (first come, first served), the whims or enthusiasm of the investigator, or any number of more or less important factors, including the full or empty condition of the office candy-jar. Many who describe new species must do so in spare time and must await convenience.

The method of approach may vary from laboratory to laboratory, from mineralogist to mineralogist. The method chosen will usually be the one that is most likely to result in an accurate identification in the minimum amount of time. Efficiency has its rewards; if the mineralogist is efficient he is able to move on to the next challenge sooner.



In practice, most laboratories rely on X-ray identification by the powder method as the initial sophisticated approach; this yields a crystallographic "fingerprint" of a sort. Alternatively, a scientist in a laboratory with a very convenient spectrographic analysis instrument may choose to obtain a "spec" analysis first; this tells which elements are present in the unknown. One who relies primarily on optical data may choose an optical approach. Here, too, the choice of method may depend upon convenience; if the investigator is engaged in much X-ray work, it may be more convenient to put the unknown with the samples to be X-rayed than to set-up for just one "spec" analysis, and vice versa.

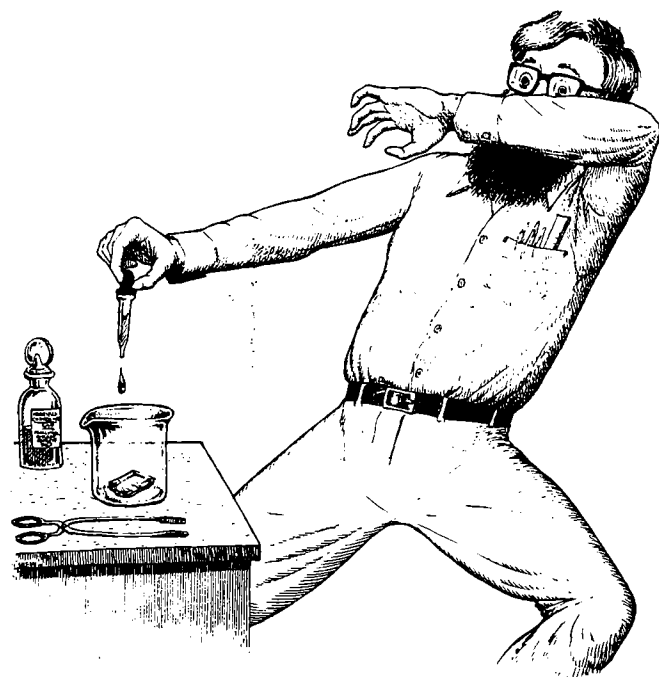
Assuming that the powder X-ray method is chosen, as it frequently is here at the National Museum, one crystal fragment of the unknown is removed and examined under the microscope in an immersion oil, for possible inclusions, inhomogeneity, twinning, and other subtle features. During this initial examination, a crude estimation of index of refraction and other salient optical features is also made. The crystal is then powdered, irradiated with X-rays of known wave-length, and a "pattern" is obtained of d values, which are then ranked in order of decreasing intensity. For a comprehensive explanation of the X-ray method, see *The State of the Art: X-ray Crystallography-Part III. The Powder Method*, (Arem, 1972).

Returning to our data obtained from the powder method, we now have a list of figures representing interplanar spacings (d) for the unknown mineral and have arranged them according to rela-

tive intensity. Hence the data may appear as:

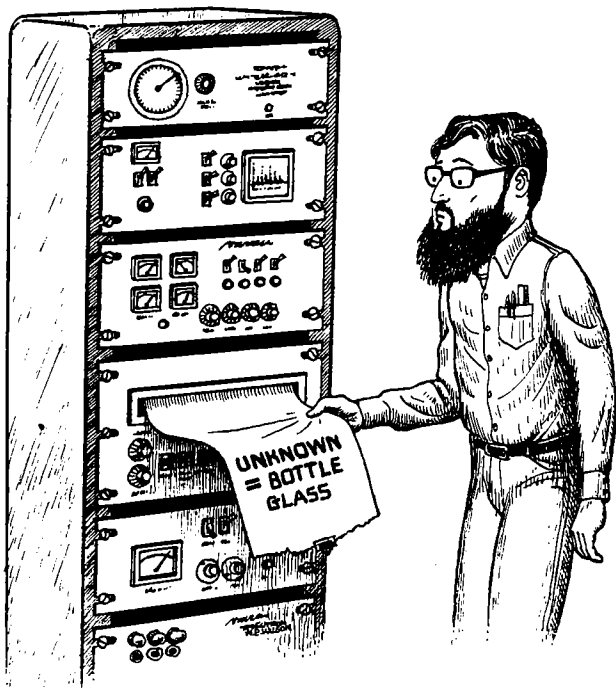
$d(\text{\AA})$	Intensity
4.850	100
3.145	85
4.336	78
7.190	78
3.480	75
2.665	63

These spacings, also called "lines" or "d's" are then sought-for in the standard X-ray reference works in hope of finding a compound or mineral whose spacings match those of the unknown. Our search may be firstly centered on the JCPDS (Joint Committee on Powder Diffraction Standards) *Search Manual for Selected Powder Diffraction Data for Minerals*. Failing to find mineral data matching that of our unknown, we might then turn to the JCPDS *Search Manual for Inorganic Compounds* which contains all known reliable powder data for inorganic compounds, most of which have not yet been discovered as minerals. In addition, one would search in all other available compilations



of X-ray powder data, some privately published. Many laboratories also maintain special files of powder data on minerals for which no data has been published and on their own unknowns, and these may be consulted as well. Usually this process leads to a known mineral but the powder data *alone* are not a truly definitive identification inasmuch as it gives us only a "fingerprint" of the structure. Different minerals may give almost identical diffraction patterns, as is the case with datolite and herderite, gypsum and pharmacolite, etc., etc., *ad confusiam!* Hence, all other determinations must be taken into account in the process of identification and verification. Most frequently, the X-ray pattern of an unknown will, if it does not lead to an identification, at least lead us to related species. For example, if the data suggest beudantite, but do not match the data for beudantite perfectly, one would then compare the data for the other members of the beudantite group: corkite, hidalgote, hinsdalite, kemmlitzite, svanbergite, weilerite, and woodhouseite. If our data then still suggests beudantite as the most likely candidate, one must still proceed with caution for other chemically dissimilar minerals such as beaverite give a similar pattern.

The above discussion could be continued at great length. The procedure outlined above is but a microcosm of the arduous



task of surveying all the available X-ray data; a procedure which may take 10-15 hours for a particularly difficult problem!

CHEMISTRY


If the unknown has endured this much scrutiny and remains unknown, the heart of the investigator beats a little faster and his enthusiasm takes a distinctly perceptible jump. The possible new mineral is next subjected to a preliminary chemical investigation to determine its chief constituents and, if possible, their relative proportions. In most cases, the mineral is subjected to a spectrographic analysis to determine which elements are present. As an alternative, especially where there is too little material for a "spec" analysis, we may "scan" the mineral with the electron microprobe, but this will not give us any proof of the presence or absence of elements with atomic number below 9. Hence, lithium, boron, carbon, and beryllium would not be detected by microprobe but would be by a spectrographic analysis. The quantity of material available for this analysis sometimes determines which method is to be used, for the probe is non-destructive.

With X-ray data and chemical components in hand, the mineralogist now has the information needed to either identify the mineral as a known species, or to ascertain that it is indeed a naturally occurring, inorganic crystalline substance possibly found for the first time in the earth—a new mineral!

Considering the first possibility, the failure to identify the mineral earlier in this sample sequence of events could have been due to a number of factors. It might be a mineral which was originally poorly described, or for which X-ray data had never been published (there are many), or perhaps it was only known before in the metamict state. Regardless of the reasons, if the mineral now has been identified, a note can be published in the literature to clear up the confusion or supplement the data for the species.

Let us now return to a mineral which is still unknown. For the sake of discussion, let us assume it is a copper sulfate mineral. Armed with the preliminary chemistry and the X-ray data one must look up the powder data for all known copper sulfate compounds, natural or man-made, in the *JCPDS Search Manual for Inorganic Compounds*, this time using the volume that is arranged by chemistry. If this attempt at identification is unsuccessful, we can proceed on the assumption that we have a new mineral.

A rigorous attempt must now be made to characterize this substance as comprehensively as possible. The composition, crystallography, optical and physical properties, locality, paragenesis, mode of occurrence, salient and subtle features, and relationship to other known species, must all be determined as accurately as possible, and the mineral should be given a name. The effort is often multi-pronged; a chemist may be pursuing the composition quantitatively, a crystallographer may be ascertaining the crystallographic constants, and a descriptive mineralogist may be pursuing the rest. In spite of the approach methods, or order of their initiation or completion, the first



*He
must then resort
to more
sophisticated techniques.*

move is to the library and a careful, meticulous perusal of the literature to date.

THE LITERATURE

A vital and extremely important part of any scientific research effort is the examination of previous work on the subject at hand, related efforts, and their relationship to the problem under investigation. For the purpose of discussion, let us assume that we are investigating a probable new mineral which is a copper sulfate occurring in the oxidized zone of a lead-copper deposit in Massachusetts and which, by the similarity of X-ray powder patterns, composition, and mode of occurrence seems likely to be related to langite and posnjakite; both of which are basic hydrated copper sulfates.

When seeking references on mineral matter, the first place to look is in *Mineralogical Abstracts*, which abstracts most papers dealing with minerals back to 1920. Since we are examining a copper sulfate, as described above, from a now defunct mine in western Massachusetts, one should examine the indices to the above publication under headings of copper sulfates, langite, posnjakite, ktenasite, Massachusetts, and other such possible related topics. This effort will result in a list of related papers which must be read, and which lead in turn to other papers possibly pertinent to the present investigation. Aside from *Mineralogical Abstracts*, the elements present in our mineral should be sought for in the indices to *Chemical Abstracts* and these sought-for references lead in turn to others and on and on. Additional references may be sought for in regional bibliographies. All available references on mining in the locality in question (in this case, Massachusetts) and papers on the local geology, hydrology, and the history of local mining efforts must be accumulated, read, distilled, and assimilated. A perusal of several references on the paragenesis and formation of deposits similar to the one in which the mineral occurs might be most helpful. The possibility still exists that knowledge about our "new mineral" is roosting somewhere in the literature as a badly described and poorly characterized substance. Special attention must be paid to the existence of any poorly characterized species, especially those for which X-ray or chemical data are missing or doubtful. References to these are usually found in the *Chemical Index of Minerals* by Hey (1962) and subsequent appendices (1963, 1974), *The System of Mineralogy* by Dana (1896), *The System of Mineralogy* by Palache *et al.* (1944, 1951), *Der Handbuch der Mineralchemie* of Doelter (1912-1931), and *Der Handbuch der Mineralogie* of Hintze (1904-present), to name but a few, and the best. Additional references must also be sought on secondary mineralization in such a de-

posit, the possible synthesis of the compound under investigation, possible industrial applications or uses for the compound, and work on similar crystal structures. If the compound has been previously found as a synthetic, the characterization is greatly facilitated.

The above is but a guideline. Special problems suggest and require special efforts and there is no one easy format. It is only to acquaint the reader with the magnitude of the task that this much has been written here.

Having thus compiled and read the related literature, one armed with a knowledge of what is known and what is not known, and the time is at hand to begin the characterization of a new mineral.

THE DESCRIPTION

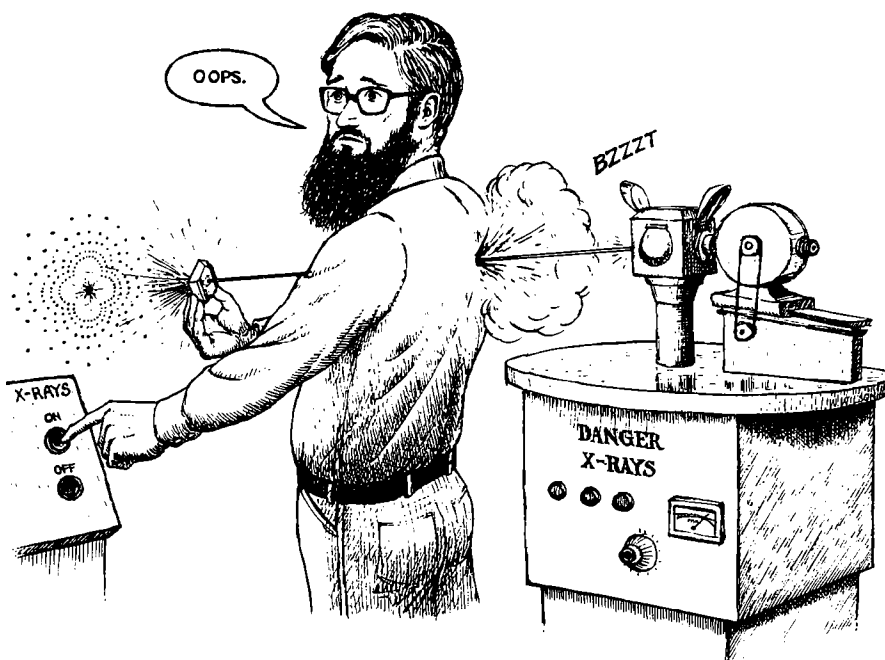
Describing a new species is sometimes a one-scientist operation but, increasingly, more and more minerals are characterized by several scientists working in cooperation with each other. In some cases, one may do the chemistry, another the crystallography, and another the physical description, etc. The following division of the complete description into discrete steps

new mineral are usually analyzed at the same time as "control" samples of known similar composition.

Electron microprobe analysis has many advantages; in addition to being non-destructive, it permits the detection of compositional zoning over areas only 10-20 microns in width, and most importantly, allows the mineralogist to analyze samples which were too tiny for analytical work just a few years ago. The microprobe and scanning electron microscope are valuable tools to the modern mineralogist, and are essential in characterizing the extremely minute crystals which comprise most new species. For a detailed explanation of these instruments, the reader is referred to *The State of the Art: The Electron Microscopes and Electron Microprobe* (Wilson, 1972).

The process of microprobe analysis involves the comparison of the composition of our mineral with the accurately known compositions of standards containing the same elements. The selection of standards for uncommon elements must be made with great care, with careful cross-checking of compositions and any possible inhomogeneities. Complex and tedious mathematical corrections for fluorescence, backscatter, and absorp-

*The mineralogist
must work
with
potentially hazardous
equipment.*



is, of necessity, quite arbitrary. Each mineral is different and special problems require special approaches. When one considers that most of the "easy" minerals have already been described (although there are several new "easy" ones found each year), what remains may be very complex minerals requiring an enormous amount of time and effort to unravel. The chemical composition and the crystallographic data are the two most important things required to characterize a new species. The other "parts" considered here are also important, but slightly less so.

THE CHEMICAL COMPOSITION

The spectrographic analysis of the new mineral has revealed which elements are present, and may have also indicated their approximate relative abundance in the mineral. It now remains to ascertain, as precisely as possible, the exact proportion of each measurable element in the new mineral. Ideally, this would be done by a wet-chemical analysis but the paucity of material frequently dictates that other methods must be used. In cases where only a few microcrystals exist, non-destructive techniques are required. Even wet-chemistry may present problems requiring special techniques. With any method samples of the

tion in the sample can now be made with computers, and are quite reliable. Other analytical methods, including atomic absorption, flame photometry, ion microprobe, etc., may be used for certain light elements. The final analysis must represent, as accurately as possible, the true composition of the new mineral. The methods used to obtain it must be stated together with any variation which may be present, accuracy of the determinations, and real and idealized formulas.

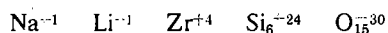
The analyses are usually presented in terms of oxides in weight percent; otherwise as elements by weight percent. This facilitates comparisons with the literature since older analyses were done wet-chemically and often the results were published as the precipitated oxide. For example, such an analysis, obtainable by diverse methods, would be given as $\text{Li}_2\text{O} : 2.8\%$, $\text{Na}_2\text{O} : 5.9\%$, $\text{ZrO}_2 : 21.84\%$, $\text{HfO}_2 : 0.50\%$, $\text{TiO}_2 : 0.75\%$, $\text{SiO}_2 : 68.24\%$ = Sum 100.04% (Table 1, column 2). Our next step is the calculation of the tentative, or empirical formula. Any mineral formula is, of necessity, tentative until a determination of the crystal structure has been made. Tentative formulas are usually given in the format suggested by the structure of related minerals.

The analysis can be stated in terms of the number of atoms

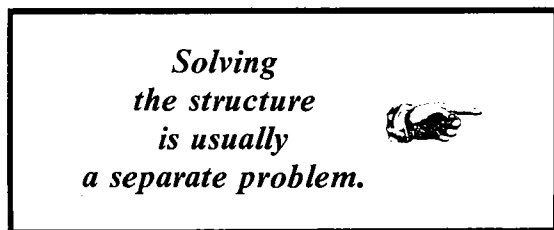
and a formula written. (In this example the idealized formula is $\text{LiNaZrSi}_6\text{O}_{15}$.) Most frequently, the number of cations is adjusted based on a fixed number of anions, such as 15 oxygens in the above example.

The above formula and its derivation represent a very simple case. Ionic substitution is common in minerals, and minerals with rather straight-forward "clean" chemistry are not often encountered. Among the other complications is the possibility that some cations, for example, iron and manganese, may exist in several oxidation states within the same mineral and this cannot be detected with the microprobe. As a result, the true nature of such compounds might not be known until the oxidation state of all elements has been determined, and the structure has been determined.

Mineral formulas must be electrostatically neutral. The positively charged ions must balance the negatively charged ions. In the case cited above, the ionic charges do balance, as shown below:



Other problems also exist, such as extensive simple ionic substitution (e.g. Mg^{+2} for Fe^{+2}), or coupled ionic substitution (involving ions of differing charge) in which there may be two substitutions taking place simultaneously to ensure electrostatic



neutrality. For example, in mixtures between dravite [$\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH},\text{F})(\text{OH})_3$] and uvite [$\text{CaMg}_3(\text{Al}_5\text{Mg})\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH},\text{F})(\text{OH})_3$], there is a concomitant substitution of magnesium⁺² for aluminum⁺³ to compensate for the substitution of calcium⁺² for sodium⁺¹.

The above section is admittedly oversimplified, much more could be written but is not necessary to give the reader an overview of the procedure and the elementary methodology. Suffice to say that the determination of the composition of every new mineral is a rather unique experience, full of potential pitfalls, and one must proceed very, very carefully. For a more detailed exposition of procedure, the reader is referred to the work of Hey (1939). Another part of the chemical description is determining the solubility of our mineral in acids or alkalis, characteristic reactions, its behavior when heated, the melting point, etc.

Not *all* of the foregoing topics are *necessary* for the description of a new mineral species; but where possible, it is best to describe the mineral as completely as possible.

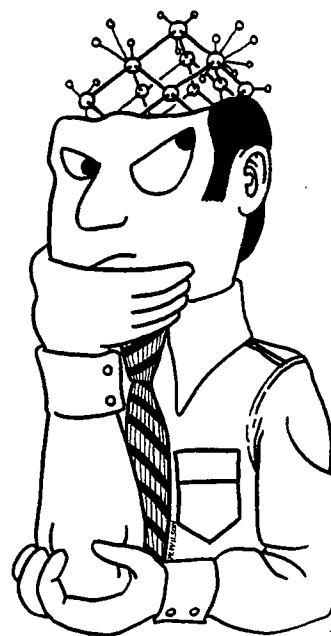
THE CRYSTALLOGRAPHY

The crystallographic part of the description of a new mineral can be simplified for the sake of this discussion, and divided into two sections: the morphological crystallography and the X-ray crystallography.

MORPHOLOGY

The word morphology means the study of shape, and the first part of the description should include very basic information such as size (in mm or cm), habit (blocky, stout, acicular, etc.),

and the axial orientation of any tabularity or elongation. All salient and latent features of the crystals should be noted with great care and precision. Examples of such features include the luster of the crystal faces, the degree of perfection of the crystals, whether they are euhedral, anhedral or subhedral, any obvious hemimorphism, any apparent dissolution and the evidence for it (rounded edges, etc.), etch pits and their orientation and symmetry, striations and their orientation, selective coloration or encrustation of stains or solid mineral matter, etc. This section of the description is most important, but is receiving less attention as the years go by and mineralogists, trained in advanced techniques, forget or omit precise physical descriptions based on visual observations. Nothing is too trivial to be included in the crystal description. If the crystals are visually attractive or basically ugly, that too is part of their description and must be included. If they visually resemble crystals of another species, that, too, must be noted.



The morphological description should also include a listing of the forms present on the crystals, their relative dominance, perfection of development and, in some cases, relative rarity. It is here that differential lusters on different forms should be carefully noted. Forms should be given in terms of their Miller indices, and may also be noted by the form names.

The absence as well as the presence of features such as those cited above should be included in any complete description, but seldom is today. This is indeed unfortunate for the reader of the description is given less information, and has no way of knowing if features not mentioned were absent, or simply not noted. Variation in the appearance and habit of crystals from different specimens, or such variation in association with certain other minerals, must be noted with care. If the mineral occurs as massive chunks or coatings instead of, or in addition to, fine crystals, this should be very carefully noted. In the absence of crystals, extreme detail should be given to the massive material including, but not limited to, its texture, cohesion or friability, toughness, parallelism or randomness of individual grains, and any other salient or latent features which aid in recognizing the mineral. Assuming that the crystals are euhedral, crystal drawings, photographs, or sketches should be included. The projection constants and an angle table might be calculated. Aberrations of form development which are best expressed in

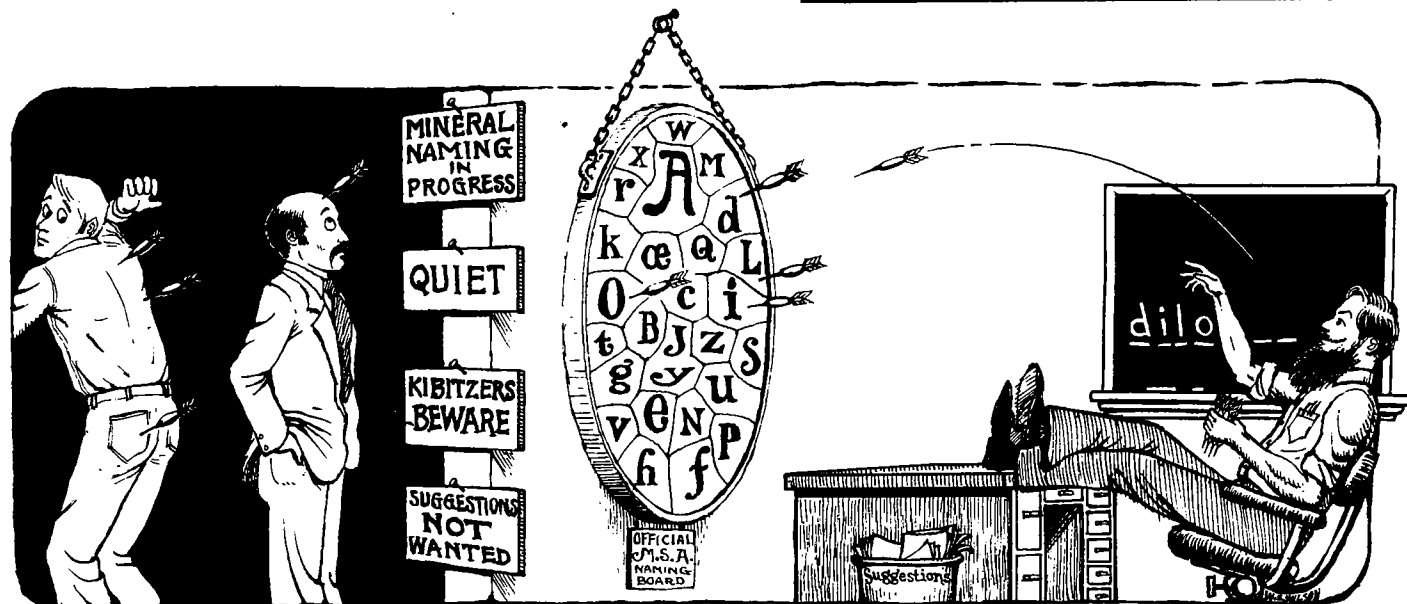
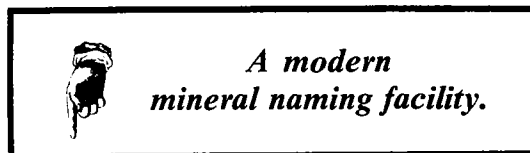
terms of forms or zones may be included here. Twinning of crystals, if obvious from external morphology, should be noted with maximum precision. The type of twinning, composition plane, or axis of revolution should be carefully noted along with any new physical description warranted by the shape of the resultant twinned crystals.

X-RAY CRYSTALLOGRAPHY

Morphological studies may sometimes serve to establish the point-group symmetry, but a detailed single-crystal X-ray study is usually required to establish the true crystal system, symmetry, space group and precise unit-cell constants (the dimensions, symmetry, and angular relations). Several different methods may be used to make these determinations and the procedure can be extremely arduous. The reflections evidenced by peaks or lines on the X-ray powder pattern are indexed on the basis of the determined cell constants, and the observed and calculated values must agree to within small limits of error. Twinning noted by X-rays but not evidenced by morphology or optical study should now be described as comprehensively as possible.

slides or cleavage surfaces of one of the known standard hardness minerals, and by other methods.

The density determination is very important and must be very carefully done. If the mineral occurs in clean pure grains from 10-25 mg, the determination can be made with a Berman balance, employing a temperature correction. If this is not possible, the density can be ascertained by flotation in Clerici's Solution, a mixture of thallium malonate and thallium formate. The liquid is diluted with distilled water, with the attendant lowering of density, until our mineral grain is suspended at equilibria in the solution. A plot of the density of this solution vs. its index of refraction is a straight-line graph and one can measure the index of refraction of the liquid with a refractometer and obtain an accurate density for the mineral. The use of heavy



A final refinement of the cell parameters obtained by single-crystal X-ray methods is accomplished using the data obtained from the powder method or single crystal diffractometer, or a back-reflection Weissenberg camera. This is usually done with the assistance of computers by least-squares refinement of a series of precise measurements of diffraction angles made by a variety of specialized techniques.

Although the solution of the crystal structure is *not* essential to the characterization of a new species, it is the most accurate statement on the true nature of the mineral. Any formula must be considered to be tentative until the crystal structure is determined.

PHYSICAL PROPERTIES

The determination of luster (both of cleavage planes and fracture surfaces), streak (when powdered for x-ray), and color is observational and not too complicated. Although there is no single agreed-upon standard system for describing color, the color charts of the Royal Horticultural Society in London and the color charts of the Geological Society of America are sometimes used. Relative hardness can be estimated easily only when the crystals are large. For microcrystals, more ingenious methods must be used, including Vickers micro-hardness testing instruments, the use of micro-chips of known minerals affixed to needles by epoxy, the rubbing of the new mineral between glass

liquids for flotation tests is quite extensive and with this method, the density of the liquid can be checked with a Westphal balance. Density determinations for minerals too heavy for the flotation method and occurring in crystals too small for the hydrostatic method may be estimated by the rate of sinking relative to that of known standards or by using a pycnometer.

And now a moment of truth has come; for the calculated and measured densities should match within a small error. The formula for calculating the density of our mineral is:

$$\frac{\text{Total molecular weight} \times Z \times 1.66}{\text{cell volume}}$$

The total molecular weight is simply the sum of the atomic weights of the elements in the formula. "Z" is the number of formula-units in the unit cell, and is usually a small whole number which is in accordance with the space-group symmetry of the mineral. The figure 1.66 is the reciprocal of Avogadro's number and cell volume is the volume of the unit cell, determined by simple geometry, and expressed in cubic angstrom units (\AA^3). A substantial disparity between the calculated and observed density values suggests an error either in the observation of the density, or the experimental work to date, and demands a scrupulous rechecking of the data.

Cleavage observations are rather straightforward but extremely small crystals may pose special problems in orientation,