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THE RELATION BETWEEN "LIGHT WOLFRAMITE" AND COMMON WOLFRAMITE

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ABSTRACT

A variety of the mineral wolframite (Fe, Mn)WO_4 with a density of 5.14 g/cm^3 and chemical composition almost identical with the normal mineral of density 7.4 g/cm^3, was reported to be found in Liquinaste, Argentina. A complete X-ray diffraction study of both varieties of the mineral showed that the only explanation was the existence of pores of submicroscopic size in the crystals of "light wolframite". This was confirmed by electron micrographs which showed pores of an average diameter of 0.3 microns. A possible statistical substitution of cations by water molecules, previously suggested by other authors, has been discarded.

INTRODUCTION

E. Kittl reported in 1951 the existence of a variety of the mineral wolframite found in Liquinaste, Jujuy, Argentina. This iron wolframite had a density of 5.14 g/cm^3 compared with 7.3 g/cm^3 of the common mineral.

A chemical analysis of the sample (Kittl, 1951) suggested $Fe_2O_3 \cdot 2WO_4 \cdot \frac{1}{2}H_2O$ as the chemical formula. However, assuming the iron oxide to be present as ferrous iron oxide, the formula of the normal ferberite plus some water was obtained. A comparison of the chemical composition of the "light wolframite" published by Kittl and that of common ferberite, given in Dana's System of Mineralogy, is shown in Table 1. It is clear that the differences are too small to account for the observed difference in specific gravity.

Later work, including an X-ray study of the sample (Kittl, 1960; Kittl and Kittl, 1965) suggested that a statistical substitution of cations by water molecules could explain both the chemical analysis and the specific gravity values obtained, in such a way that the "light wolframite" would have FeO replaced by H_2O in 30 percent of the unit cells. According to these authors no pores larger than 20 Å could be observed with the electron microscope.

We thought that, if the mentioned substitution existed, it should be possible to detect it by means of an X-ray study of the crystal structure of both the normal and light wolframites.

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Table 1. Chemical Analyses of Normal and "Light" Wolframites, (Weight Percent)

	(1)	(2)	(3)	(4)	(5)	(6)
WO_3	74.28	75.07	69.60	73.6	74.82	76.76
FeO	1.62	22.54		20.28	22.47	21.12
Fe_2O_3	21.18		23.27			
MnO	1.30	1.41	1.07	1.21	1.15	1.26
MgO		0.18	1.45	0.82	1.56	0.85
CaO			0.37			
H_2O	1.31		0.24	0.05		
ZnO			0.02	0.01		
SiO_2		0.88	0.65	0.22		
$(Nb, Ta)_2O_5+SnO_2$			3.23	3.65		
Total	99.69	100.08	99.9	99.8	100.0	99.99
Sp. gravity g/cm$_3$	5.14	7.283	5.17	7.14	5.17	7.14

(1) Light wolframite, from Liquinaste, Jujuy, Argentina (Kittl, 1951)

(2) Ferberite, from Riddarhyttan, Sweden (Assarson, 1923, in Palache, Berman, and Frondel, 1951)

(3) Light wolframite, from Liquinaste, Jujuy, Argentina, used in this work. Analyst: María Karpisek.

(4) Normal ferberite, from Liquinaste, Jujuy, Argentina (Cid-Dresdner and Escobar, 1968), Analyst: María Karpisek.

(5) and (6) same as (3) and (4) respectively, recalculated for (Fe, Mn, Mg)O WO_3

Methods and Results

Crystals of both varieties of wolframite were kindly provided by Professor E. Kittl, Buenos Aires, Agrentina, to be used in this study.

Determination of the specific gravity of several pieces of the Liquinaste sample by the pycnometer method showed the existence of a range of values from 5.17 to 7.4 g/cm^3. Samples having the two extreme values of density were chosen for chemical analysis.

The sample with a density of 7.3 g/cm^3 consisted of a large single crystal, 4 to 5 cm long, with well-developed faces. Before sending it for chemical analysis, a small piece was detached and used for the determination of the cell parameters and intensity measurements. The "light wolframite" sample had a more massive appearance and consisted of two pieces, the density of each piece was measured and yielded a value of 5.17 g/cm^3. A small part detached from one of those pieces was used for X-ray measurements.

The results of both chemical analyses, given in Table 1, agree closely with that formerly reported by Kittl, with the exception of the water content in the "light" sample. This fact was important in relation with the substitution proposed. Both samples can be classified as ferberite, the iron rich end member of the series of the wolframites, since the FeO weight percent content is greater than 18.9. The unit cell content of heavy ferberite was found to be $(Fe, Mn, Mg)_2W_2O_8$, while that of the lighter material was $(Fe, Mn, Mg)_{2.21}W_{1.91}O_8$. The last formula was obtained assuming that all the iron oxide present was ferric iron oxide (the chemical analysis could not tell how much of each was included), and the corresponding calculation has to be considered as less reliable than the former one.

TABLE 2. UNIT CELL CONSTANTS OF "LIGHT FERBERITE" AND NORMAL FERBERITE

	a (Å)	b (Å)	c (Å)	β	Space group
Light ferberite	4.753	5.720	4.968	90° 5′	$P2/c$
Normal ferberite	4.750	5.720	4.970	90°10′	$P2/c$

The unit cell constants for the light and heavy ferberite were determined by precession and Weissenberg methods, and are listed in Table 2. The differences on cell edges and angles are within the limits of error of the precession method, which is the more exact of the two methods used (Buerger, 1964).

A complete structure determination was carried out for both samples. Both structures were solved by vector and Fourier methods (Buerger, 1960). Since the dimensions of the unit cell were favorable to work on projections, only the $hk0$ and $h0l$ intensity data from integrated precession photographs were used. These data proved to be sufficient to solve and refine the structures.

In the (010) projection, the positions of the W and Fe atoms are fixed by the space group. The R factors for the $h0l$ reflections, considering only these two atoms, were 0.138 and 0.14 for the normal and light ferberite samples, respectively. In the (001) projection the x coordinates for W and Fe are also fixed by the space group. The y coordinates for W and Fe are also fixed by the space group. The y coordinates of these atoms were adjusted until the R factors were 0.14 and 0.145 for the normal and light ferberite crystals respectively. The refined position of these two cations were the same within the experimental error for both structures.

Difference Fourier syntheses $\Delta\rho_1(xz)$ and $\Delta\rho_1(xy)$, using $F_{obs}-F_{cal}$ as coefficients with signs determined by the W and Fe atoms, were then calculated for both samples. The position of the oxygen atoms were determined from these projections.

A complete account of the solution and refinement of the normal ferberite structure is given elsewhere (Cid-Dresdner and Escobar, 1968). An analogous procedure was followed for the solution of the light ferberite structure. The similarity of the results in both cases makes unnecessary to give here the intermediate steps.

The final difference Fourier projections $\Delta\rho_2(xy)$ and $\Delta\rho_2(xz)$ for light ferberite are shown in Figure 1.

ESTIMATION OF ERRORS IN THE ATOMIC COORDINATES

The standard errors in the atomic coordinates of normal and light ferberite were estimated from the difference Fourier maps using the method of Lipson and Cochran (1953).

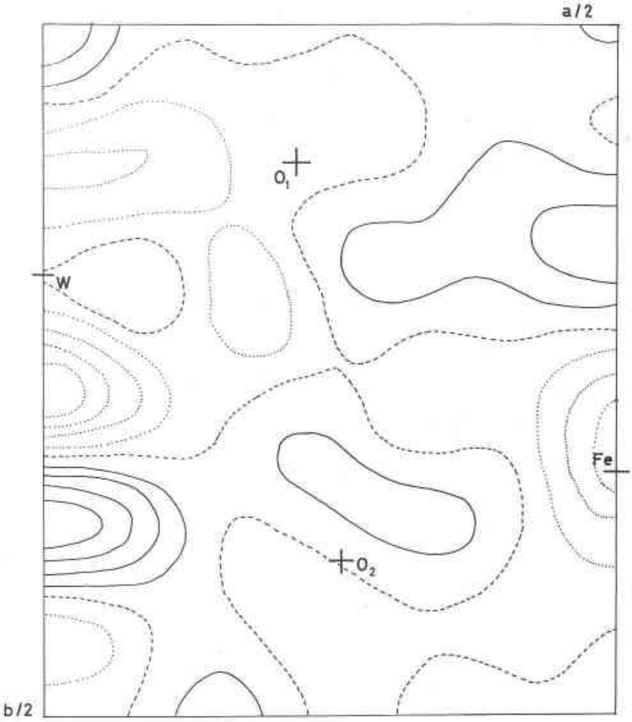
In this method the standard error σ of an atomic coordinate x of the nth atom is given by the relation:

$$\sigma(x_n) = \frac{\left\{\overline{\left(\frac{\partial D}{\partial x}\right)^2}\right\}^{1/2}}{C_n}.$$

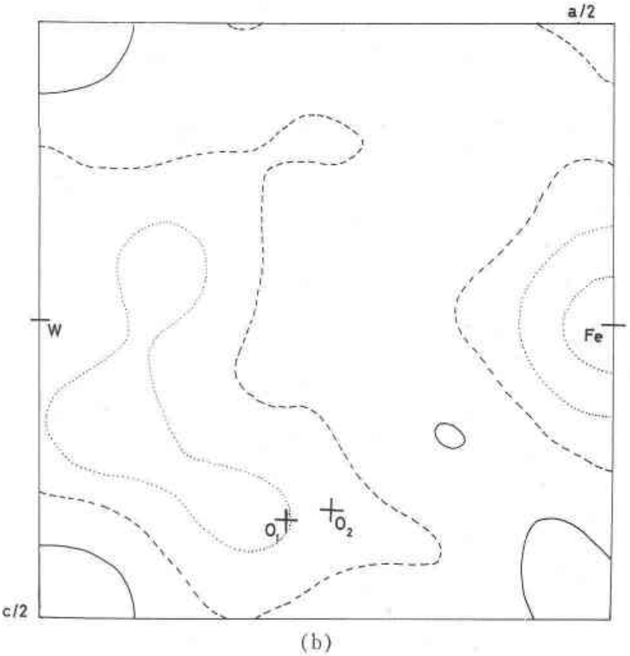
The meaning of the symbols is the following:

$$D = \rho_0 - \rho_c \qquad (=\Delta\rho \text{ in this work})$$

$$C_n = \frac{\partial^2 \rho_c}{\partial x^2}$$



(a)



(b)

ρ_o and ρ_c are electron density functions calculated with F_{obs} and F_{cal} respectively as coefficients for the Fourier summations.

In practice $\partial^2\rho_c/\partial x^2$ was replaced by $\partial^2\rho_0/\partial x^2$, which is the central curvature of the nth atom as measured on the F_{obs} synthesis. The approximation of Costain and Booth for the electron density function was also used, as suggested in the method, yielding

$$\rho_0 = Z\left(\frac{p}{\pi}\right)^{3/2} \exp\,(-\mathrm{p}r^2), \quad \text{and} \quad \frac{\partial^2\rho_0}{\partial x^2} \approx 2\mathrm{p}\rho_0, \quad \text{where} \quad \mathrm{p} \approx 5.0$$

The gradient $\partial D/\partial x$ was evaluated from the separation of the contour lines near the location of the center of the atoms on the $\Delta\rho_2(xy)$ synthesis. The *c* axis projection was selected because it contains the only variable coordinate of the W and Fe ions and it does not present superimposed atoms. For identical reasons C_n was estimated from the (001) projection of the electron density functions.

Only one standard error was calculated for the three coordinates of each oxygen atom, since they are considered as spherically symmetric. The gradient $\partial D/\partial x$ for the oxygen atoms was the average of measurements taken in the directions of the *a* and *b* axes. For the W and Fe atoms, $\partial D/\partial x$ was measured in the direction of the *b* axis.

DISCUSSION OF THE RESULTS

A comparison of the final atomic parameters and reliability factors *R* for the structures of "light" and normal ferberite is given in Table 3. The structures are identical within the limits of the errors of the methods used. The maximum differences between both structures was found in the oxygen coordinates and was 0.005. This difference is of the order of magnitude of the minimum error in the measurements of the cell edges (Buerger, 1964), and ½ of the minimum error in the oxygen coordinate measurements.

If light ferberite could be considered to be a substitutional structure of normal ferberite as suggested previously (Kittl, 1960) one would expect to find differences in bond lengths and bond angles that would directly affect the unit cell and distort the structure. None of these differences could be detected in this work, beyond the error of the method used.

Since the substitution proposed was a FeO group by a water molecule on 30 percent of the unit cells, one would expect to find differences in the ratios of the tungsten and iron peaks in the final electron density maps. This was not detected, the ratios being 4.25 for light ferberite and 4.32 for normal ferberite, on (010) projections. This projection is free of errors in the atomic coordinates of both cations.

Even if one accepts that the structures are the same, there is a significant difference in the degree of refinement attained. The refinement of

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FIG. 1. Final difference Fourier syntheses $\Delta\rho_2(xy)$ and $\Delta\rho_2(xz)$ for light ferberite. The coefficients were $F_{obs}-F_{cal}$. Contours at intervals of 1.8 e/Å^1.

TABLE 3. FINAL ATOMIC PARAMETERS AND RELIABILITY FACTORS OF THE STRUCTURES OF "LIGHT FERBERITE" AND NORMAL FERBERITE

Atom	Parameter	Light ferberite	Normal ferberite
W	x	0	0
	y	0.1808 ± 0.002	0.1808 ± 0.002
	z	1/4	1/4
	B (Å^2)	0.20	0.20
Fe	x	1/2	1/2
	y	0.3215 ± 0.005	0.3215 ± 0.005
	z	3/4	3/4
	B (Å^2)	0.45	0.40
O (I)	x	0.2167 ± 0.010	0.2158 ± 0.010
	y	0.1017 ± 0.010	0.1068 ± 0.010
	z	0.5833 ± 0.010	0.5833 ± 0.010
	B (Å^2)	0.6	0.6
O (II)	x	0.2583 ± 0.014	0.2623 ± 0.012
	y	0.3900 ± 0.014	0.3850 ± 0.012
	z	0.0900 ± 0.014	0.0912 ± 0.012
	B (Å^2)	0.6	0.6
	R_{hk0}	0.114	0.072
	R_{h0l}	.072	0.054

the "light ferberite" sample stopped at $R_{hk0}=0.11$ and $R_{h0l}=0.07$, whereas for the normal ferberite the values were $R_{hk0}=0.072$ and $R_{h0l}=0.054$. Since the reproducibility of the integrated intensity data, film recorded and measured on a Kipp microdensitometer, was estimated to be of the order of 7 percent, the R_{hk0} of the "light ferberite" seemed to be too high.

In order to search for possible differences on both structures which could explain the different degree of refinement obtained, two special "difference Fourier" syntheses were calculated. The coefficients used were the difference in the observed values of the structure factors of normal and light ferberite. These two projections $\Delta\rho'(xz)$ and $\wedge\rho'(xy)$ are shown in Figure 2.

In agreement with the results previously mentioned, no observable differences were found on the $\Delta\rho'(xz)$ projection. The distribution of the

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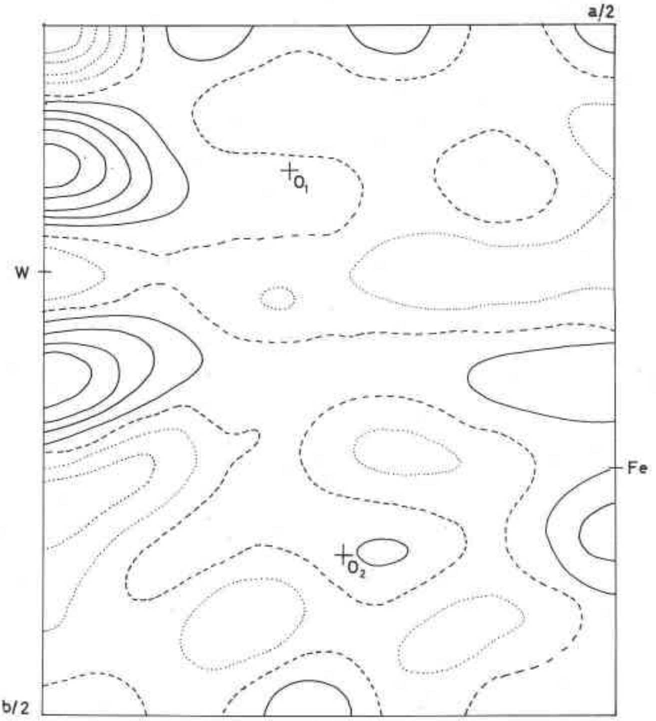
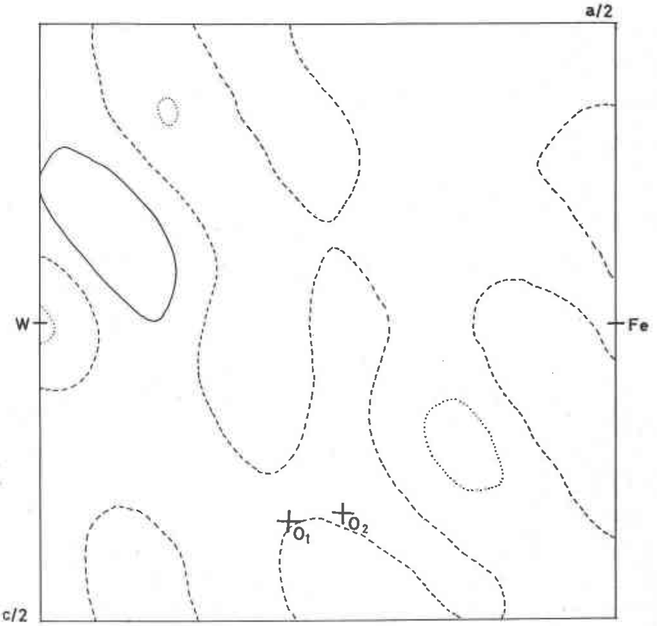
FIG. 2. Difference Fourier syntheses $\Delta\rho'(xy)$ and $\Delta\rho'(xz)$ calculated with F_{obs} (normal ferberite) $-F_{\mathrm{cal}}$ (light ferberite) and the signs obtained from the final structure factors calculation of normal ferberite. Contours at intervals of 1.8 e/Å^2.



(a)



2b

(b)

maxima on $\Delta\rho'(xy)$ resembles an anisotropic temperature effect of the W atom in the direction of the *b* axis. This effect can be satisfactorily explained as due to a lack of absorption correction on both intensity data. The dimensions of the "light ferberite" crystal were 0.04×0.12 ×0.14 mm, while those of the normal ferberite were 0.18×0.08×0.06 mm. In obtaining the *h*0*l* precession photographs, the precession axis *b* was parallel to the shortest dimension of both crystals, the spindle axis being a^* for the normal ferberite, and c^* for the light sample. For the *hk*0 photographs, the precession axis *c* was parallel to the 0.08 mm dimension for normal ferberite and to the 0.14 mm dimension for the light ferberite, the spindle axes being a* and b* respectively. It is obvious that the *hk*0 reflections on both crystals were affected by absorption in a different way. Unfortunately we did not have the computer facilities to correct for absorption in prismatic crystals (Onken, 1964).

The results reported above lead us to the conclusion that the different densities observed on these varieties of ferberite crystals cannot be explained by structural differences. The simplest explanation appears to be the existence of pores in the crystals. These pores were not observable on the optical microscope and according to the literature (Kittl and Kittl, 1965) were not observed either with the electron microscope on replicas of the surface.

Since the existence of these holes could explain the whole range of densities observable on the mineral, a new study of "light ferberite" crystals was performed using the electron microscope. Since pores had not been observed on external surfaces of the crystals, the samples were broken and replicas were obtained from the fracture surface. This surface was smooth and brilliant. When examined under the optical microscope, it showed a great variety of details but no pores could be seen.

In obtaining surface replicas the following technique was used: The fracture surface was first moistened with acetone and then covered with triafoil. Once dried, this was stripped away. The replica was covered with a deposit of uranium oxide, or chromium or palladium oxide in an evaporation chamber. These different materials were used in order to eliminate possible sources of error. The metallized surface was covered with paraffin and the preparation was next bathed in methyl acetate to eliminate the triafoil and in toluene to dissolve the paraffin. The replicas were mounted on grids and observed with a Siemens Elmiskop I.

The results are shown in Figures 3 and 4 and confirm the conclusions obtained by X-ray methods. The pores show a rather uniform distribution and have an average diameter of 0.3 microns. Their shape can be either circular or elongated. The smallest pores observed had a diameter of 0.03 microns.

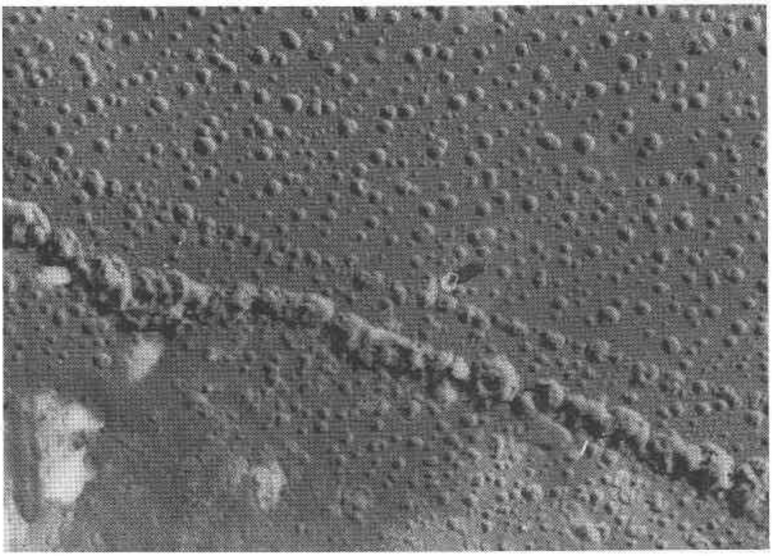


Fig. 3. Electron micrograph of a replica of the fracture surface of a crystal of "light" ferberite, ×5100. The alignment of pores is attributed to fracture after the primary crystallization, followed by a recrystallization.

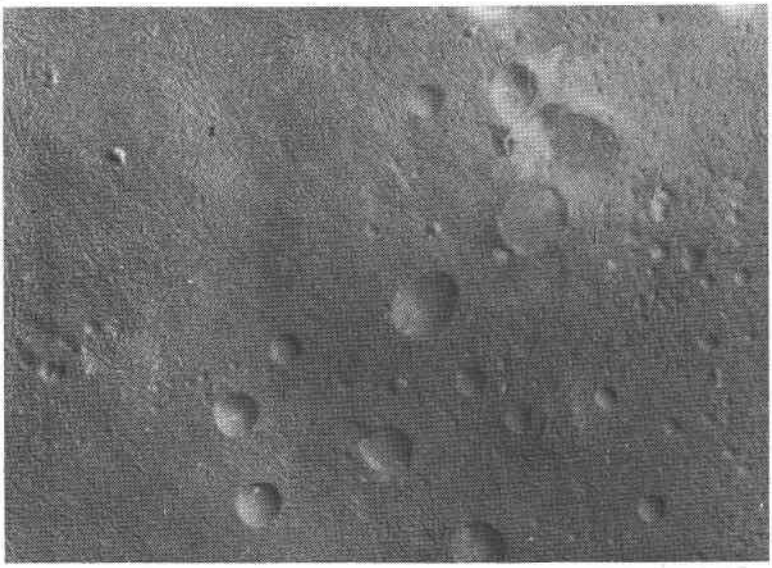


Fig. 4. Electron micrograph of a replica of the fracture surface of a crystal of "light" ferberite showing circular pores of 0.03 μm minimum diameter. Magnification ×21,500.

There is agreement in attributing the existence of pores in minerals to the presence of water and gases dissolved in the bulk material about to crystallize. These would be enclosed in the pores and would sometimes remain within them, which could explain the presence of water detected in chemical analyses of light ferberite (Nos 1 and 3 of Table 1).

It is also clear that different crystallization conditions can determine whether or not a mineral will have pores. Of the several deposits of wolframite found in Argentina, only on those of Liquinaste, Jujuy, could the light variety of the mineral be found. According to Kittl (1970), the deposits of San Luis, Córdoba, La Rioja, and Catamarca were presumably formed in the Paleozoic era. Only "heavy" wolframite is found in all of them, possibly formed from thermal solutions under great pressures and slow cooling. The deposit of Liquinaste was formed more recently, in the Cretaceous period or later. The light wolframite found there is always associated with tourmaline. The conditions of crystallization in the Liquinaste deposit were probably higher temperatures, lower pressures, and the presence of gaseous components.

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REFERENCES

BUERGER, M. J. (1960) *Crystal-Structure Analysis.* John Wiley and Sons, Inc. New York.

——— (1964) *The Precession Method.* John Wiley and Sons, Inc. New York.

BULYCHEV, D. K., B. I. BERESNEV, M. G. GADJUKOV, E. D. MARTYNOV, K. P. RODIONOV, AND JU.N. RJABININ (1964) Sur la posibilité de la suppression de pores et de criques dans les métaux au cours du processus de la déformation plastique sous forte presion hydraulique. *Fiz.Metal. Metalloved.* **18,** 437–442 [*Bull. Signal.* 6, *26*, 10189, (1965)].

CID-DRESDNER, HILDA AND CARMEN ESCOBAR (1968) The crystal structure of ferberite, $FeWO_4$. *Z. Kristallogr.* **127,** 61–72.

KITTL, ERWIN (1951) Sobre la Wolframita de Liquinaste, Jujuy. *Rev. Minera* **20,** 56–61.

——— AND PAUL KITTL (1965) Der leichte Wolframit von Liquinaste, Jujuy in Argentinien. *Aufschluss* **16,** 52–54.

KITTL, PABLO (1960) Sobre la wolframita liviana de Liquinaste, Jujuy. *Rev. Minera* **25,** 3–7.

ONKEN, HAJO H. (1964) *Manual for Some Computer Programs for X-ray Analysis.* Crystallographic Laboratory, Mass. Inst. Tech., Cambridge, Massachusetts.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *The System of Mineralogy of Dana, vol. 2, 7th Ed.* John Wiley and Sons, Inc. New York.

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