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# THE CRYSTAL STRUCTURE OF MAGNOLITE, $Hg_2^{1+}Te^{4+}O_3$

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## ABSTRACT

Magnolite, $Hg_2^{1+}Te^{4+}O_3$, is orthorhombic *Pbm*2 (No. 28), with cell parameters *a* 5.958(1), *b* 10.576(2), *c* 3.749(1) Å, and $Z = 2$. Solution of the crystal structure using 312 observed ($3\sigma$) reflections refined to residuals *R* 4.5% and $R_w$ 3.6%. The structure analysis determined the valence state of the cations and the number of oxygen atoms in the chemical formula. Each Hg is coordinated to another Hg and 4 O, and each Te has 5 O and a lone pair of electrons associated with it. The lower oxidation state of the cations is in keeping with the geological environment of the Magnolia District, in Colorado; the deposit formed at low $f(O_2)$ as evidenced by the main ore assemblage of Au, Ag and Pb tellurides in association with coloradoite, native mercury and native tellurium.

*Keywords:* magnolite, crystal structure, mercurous, tellurite, Magnolia District, Colorado.

## SOMMAIRE

La magnolite, $Hg_2^{1+}Te^{4+}O_3$, possède une maille orthorhombique, groupe spatial *Pbm*2 (no 28), et les paramètres suivants: *a* 5.958(1), *b* 10.576(2), *c* 3.749(1) Å, $Z = 2$. Sa structure cristalline a été affinée jusqu'à un résidu *R* de 4.5% et $R_w$ de 3.6% en utilisant 312 réflexions observées ($3\sigma$). L'analyse a permis de déterminer la valance des cations et le nombre d'atomes d'oxygène dans la formule chimique. Chaque atome de mercure est lié à un atome de Hg et à quatre atomes d'oxygène, tandis que chaque atome de Te est lié à cinq atomes d'oxygène et possède une paire d'électrons isolés. Le faible degré d'oxydation des cations concorde avec le contexte géologique du district de Magnolia, au Colorado. Le dépôt a été formé dans un milieu de faible fugacité d'oxygène, comme en témoigne le principal assemblage du minerai, qui contient l'association de tellurures de Au, Ag et Pb, de coloradoïte et de mercure et tellure natifs.

*Mots-clés:* magnolite, structure cristalline, mercureux, tellurite, district de Magnolia, Colorado.

## INTRODUCTION

Magnolite, first described by Genth (1877), was abstracted by Dana (1903) but was dropped from Dana's Seventh Edition (Palache *et al.* 1951). The mineral has been re-established by Roberts *et al.* (1989). Although the Hg:Te ratio of 2:1 was known by Genth, the oxidation state of the cations and presence or absence of H were not known. The author has previously demonstrated a technique for the determination of light elements and the oxidation state of cations using results of a good structure-refinement (Grice & Ercit 1986, Grice *et al.* 1987, Grice & Groat 1988); several examples were summarized by Hawthorne & Grice (1987).

Genth inferred the formula $Hg_2TeO_4$ for magnolite (Dana 1903), but he was uncertain whether the mineral is a tellurate or a tellurite. If the possible presence of H atoms is ignored, the alternative formulae are: $Hg_2^{1+}Te^{4+}O_3$, $Hg_2^{1+}Te^{6+}O_4$, $Hg_2^{2+}Te^{4+}O_4$, and $Hg_2^{2+}Te^{6+}O_5$. Taking into consideration the stability of the various cations within the Eh-pH equilibrium diagrams at 25°C (Pourbaix 1974), the most plausible formulae are $Hg_2^{1+}Te^{4+}O_3$ and $Hg_2^{2+}Te^{6+}O_5$. The stability curves for the transition of $Hg^{1+} \rightarrow Hg^{2+}$ and $Te^{4+} \rightarrow Te^{6+}$ almost overlie each other, leaving a small stability field for $Hg_2^{1+}Te^{6+}O_4$ and no stability field for $Hg_2^{2+}Te^{4+}O_4$.

## EXPERIMENTAL

Two crystal fragments from the type material collected by Genth at the Mount Lion mine, Magnolia District, Colorado, U.S.A., were used for data collection and structure determination. Only the second crystal is discussed, as it gave a better refinement of the structure owing to improved data. This crystal is a {100} plate, 0.10 × 0.06 × 0.025 mm. Single-crystal precession photographs yielded space-group choices $Pb2_1m$ (#26), *Pbm*2 (#28) and *Pbmm* (#51). Intensity data were collected on a fully automated Nicolet R3m four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated Mo$K\alpha$ radiation. A set of 25 intense reflections was used to orient the crystal and subsequently to refine the cell dimensions: *a* 5.958(1), *b* 10.576(2) and *c* 3.749(1) Å. Two asymmetric sets of intensity data were collected up to $2\theta = 60°$ using a $\theta$:$2\theta$ scanning mode with a scan range of 2° $2\theta$ plus $\alpha_1$-$\alpha_2$ separation and scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Of the 401 unique intensities collected, 338 were considered observed $[I > 3\sigma(I)]$.

Reduction of the intensity data and refinement of the structure were done by the SHELXTL package of programs. Data reduction included corrections for background, scaling, Lorentz linear absorption correction, $\mu = 724$ cm$^{-1}$ for Mo$K\alpha$ radiation, thus making this the most critical procedure in the data reduction and subsequent refinement of the structure. A set of 10 intense diffraction maxima over the range 7 to 52° $2\theta$ were chosen for $\Psi$-diffraction-vector scans after the method of North *et al.* (1968). The $\Psi$-scan set of intensity data was used to refine a planar, empirical absorption-correction. This correction assumes an infinitely thin plate. To compensate for the thickness of this plate, all diffracted rays passing through the crystal edge must be omitted from the data set. This restriction reduced the observed data from 338 to 312 reflections. The absorption correction reduced the merging *R* of the $\Psi$-scan data set from 10.1% to 2.4%.

## CRYSTAL-STRUCTURE ANALYSIS

The phasing of a set of normalized structure-factors gave a unique *E*-map with the coordinates of the two heavy atoms Hg and Te. The mean value of $|E^2-1|$ for the region $\sin\theta/\lambda > 0.15$ is 0.91, which favors the centrosymmetric space group *Pbmm*. In this space group the positional and isotropic thermal parameters of the two heavy atoms refined to give a residual index *R* of 12%. From this initial model, problems were encountered in locating the sites of the oxygen atoms. A mirror plane perpendicular to the *Z* axis imposed restrictions that gave rise to impossibly short O–O distances in such a small repeat-distance (*c* 3.75 Å). To resolve this problem, space group *P*1 was used to determine the O sites using the heavy-atom model in conjunction with a difference-Fourier map. The O sites determined are compatible with the symmetry of noncentrosymmetric space group *Pbm*2. The mean $|E^2-1|$ test indicated a center of symmetry, but this is not disturbing in light of the fact that the heavy atoms have an approximately centrosymmetric distribution.

In the final least-squares refinement, the Hg site and the Te site were refined with anisotropic temperature-factors, and the O1 site, with an isotropic temperature-factor; the O2 site had to have a fixed temperature-factor. An isotropic extinction-correction added to the weighting scheme resulted in final residual indices of *R* 4.5% and $R_w$ 3.6%. At this stage in the structure refinement the ΔF synthesis had only a minor positive residual close to the O2 site. If the temperature factor of O2 is allowed to refine, this residual disappears, but the temperature factor is disproportionately high ($U = .08$). No doubt this temperature-factor problem results from the severe absorption-corrections and the bias in data created by removing certain reflections that could not be fitted in the absorption-correction routine for an empirical plate. These effects would be amplified for the O2 site because it lies at a special position on the mirror plane. The final positional and thermal parameters are given in Table 1, and the interatomic distances and angles, in Table 2. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

TABLE 1. POSITIONAL AND THERMAL PARAMETERS IN MAGNOLITE

| Site | x | Y | z | U(eq) |
|---|---|---|---|---|
| Hg | 0.1907(4) | 0.5528(1) | 0 | 0.0237(5)* |
| Te | 0.4452(8) | 1/4 | 0.4991(27) | 0.0146(10)* |
| 01 | 0.501(10) | 0.130(2) | -0.122(5) | 0.029(6) |
| 02 | 0.734(10) | 1/4 | 0.438(8) | 0.03(0) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *UijX10⁴ | Hg | 149(11) | 210(5) | 351(7) | 59(17) | 78(33) | -44(7) |
| | Te | 96(26) | 159(10) | 182(1) | 0( 0) | 30(73) | 0(0) |

TABLE 2. SELECTED INTERATOMIC DISTANCE (Å) AND ANGLES (°) IN MAGNOLITE

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Hg-Hgk | 2.533(4) | | Hgk-Hg-01d | 107(1) | | 01c-01d | 2.74(5) |
| -01c | 2.06(5) | | 02c | 119(1) | | 01c-02d | 2.50(5) |
| -01d | 2.71(4) | | 02d | 116(1) | | 01c-02c | 2.82(5) |
| -02c | 2.69(2) | | 01c | 167(1) | | | |
| -02d | 3.00(2) | | 01d-Hg-02c | 123.6(4) | | | |
| | | | 02d | 106(1) | | | |
| Mean* | 2.62 | | 02c-Hg-02d | 82.2(4) | | | |
| | | | 01c-Hg-01d | 69(1) | | | |
| | | | 02c | 72(1) | | | |
| Hg-Te | 4.007(5) | | 02d | 56(2) | | | |
| | | | Mean | 94.5 | | | |
| Te-01o,d | 2.68(2) | x2 | 01-Te-01a,e | 108(1) | x2 | 01-02 | 2.82(5) |
| 01a,e | 1.94(2) | x2 | 01-Te-01o,d | 58(1) | x2 | 02-01a | 2.50(5) |
| 02 | 1.74(6) | | 02-Te-01o,d | 76(2) | x2 | 01-01d | 2.55(5) |
| | | | 02-Te-01a,e | 86(2) | x2 | | |
| Mean | 2.20 | | Mean | 82 | | | |

*Mean Hg-O

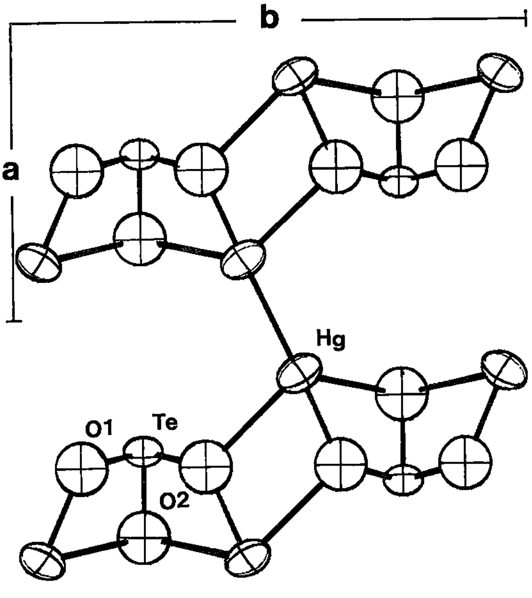

FIG. 1. A Z-axis projection of the magnolite structure.

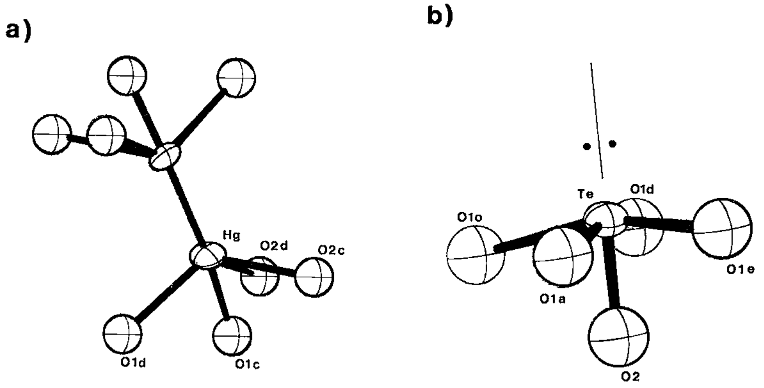

FIG. 2. Coordination polyhedra of cations in the magnolite structure. a) $Hg^{1+}$; b) $Te^{4+}$.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The unique chemistry of magnolite, mercurous tellurite, gives rise to a novel structure. Bond-valence sums were calculated for the various sites based on the constants of Brown (1981). The sums are: Hg 1.11, Te 4.08, O1 2.13 and O2 2.04 *v.u.* These calculations allow the assignment of the correct valence to each cation, $Hg^{1+}$ and $Te^{4+}$, and the conclusion that there are no protons associated with either of the two O sites. The resultant structural formula is $Hg_4^{1+}Te_2^{4+}O_6$. A *Z*-axis projection for the magnolite structure is given in Figure 1. Hg and Te polyhedra are cross-linked by both O sites. Figure 2 shows the detail of each of these interesting cation coordinations. Each $Hg^{1+}$ is coordinated to another $Hg^{1+}$ and 4 O (Fig. 2a). This diatomic $Hg^+$–$Hg^+$ bond is typical of mercurous compounds, and the bond length of 2.53 Å is in keeping with that (2.53 Å) observed in calomel (Wyckoff 1965), 2.516 Å in eglestonite (Mereiter & Zemann 1976), 2.54 Å in synthetic mosesite (Wyckoff 1965), and 2.66 Å in synthetic terlinguaite (Šćavničar 1956). The coordination polyhedron of Hg to the 4 oxygen atoms is irregular, roughly resembling a planar ring in which O1*d*, O2*c* and O2*d* surround the Hg and with an apical O1*c* opposite the apical Hg at the other end. The Hg–O distances vary from 2.06 to 3.00 Å (mean 2.62 Å). The Te coordination polyhedron may be thought of as a distorted 'octahedron' with 4 planar O on the *b*-glide plane (O1 site), apical O2 on the mirror plane, and a lone pair of electrons opposite O2 on the other apex of the 'octahedron' (Fig. 2b). The mean $Te^{4+}$–O bond length of 2.20 Å is rather large in comparison to the average of 2.14 Å for other 5-fold coordinated $Te^{4+}$ ions, as summarized by Effenberger *et al.* (1978). The large $Te^{4+}$–O mean distance in magnolite results from the two bond distances of 2.68 Å, which still must be considered in the polyhedron because each contributes 0.23 *v.u.* to the 4.07 *v.u.* bond-valence sum of Te. The lone pair of electrons creates an apparent "hole" in the magnolite structure (Fig. 1). Although there was no direct evidence of these electrons on the final difference-Fourier map, probably because of the severe absorption correction already discussed, the effect on the plane of 4 O surrounding the $Te^{4+}$ is evident in the 81° average of the four bond angles of the type O2 (apical)–Te–O1 (equatorial). This configuration compares very well to the same average angle of 82° in $TeF_4$, and 78.8° in $KTeF_5$ (Galy *et al.* 1975). Thus the lone pair of electrons can be considered as repelling the plane of 4 equatorial oxygen atoms below the $Te^{4+}$ atom, and they do not interact with any other atoms across the "hole".

## PARAGENESIS

Magnolite, the first mercury–tellurium oxide to be found in nature, occurs with coloradoite, native mercury, native tellurium, and many Au, Ag and Pb tellurides (Vanderwilt 1947) that constitute the main ore minerals in the Magnolia District. It is evident from this association that the conditions of crystallization of these minerals define a low $f(O_2)$, in the area of transition of $Hg \rightarrow Hg^{1+}$ and $Te \rightarrow Te^{4+}$. Observing this, one could have deduced that magnolite is a late-stage oxidation product of native Hg tallographic proof is reassuring. It is likely that magnolite is a late-stage oxidation product of native Hg and Te; its intimate association with tellurite and Genth's (1877) "ferrotellurite" or keystoneite (Back *et al.* 1988) supports this hypothesis.

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