# Reports

## High-Pressure Synthesis of Molybdates with the Wolframite Structure

Abstract. *A series of small cation molybdates,* $MgMoO_4$*,* $MnMoO_4$*,* $FeMoO_4$*,* $CoMoO_4$*,* $NiMoO_4$*, and* $ZnMoO_4$ *with the wolframite structure characteristic of the corresponding tungstates have been synthesized at high pressure and temperature. The high-pressure compounds revert to the ambient pressure modifications if heated in air at 600°C.*

Molybdenum and tungsten both have six electrons outside a noble-gas shell. The ion radii of $Mo^{6+}$ and $W^{6+}$ are nearly equal (*1*). One might expect that corresponding compounds with hexavalent Mo and W would have similar crystal structures. The crystal structures are similar in some compounds, but there are notable exceptions. One such exception has been the failure up to now to produce small cation molybdates isostructural with the wolframite-type tungstates, $MgWO_4$, $ZnWO_4$, $MnWO_4$, $FeWO_4$, $CoWO_4$, and $NiWO_4$.

The structure of $NiWO_4$, which is monoclinic with space group $P2/c$, is based on a distorted hexagonal close packing of oxygen atoms, with Ni and W atoms each occupying one-fourth of the octahedral interstitial sites (*2*). Since compounds with the wolframite structure would be relatively dense, we thought that some wolframite-type molybdates might be synthesized at high pressure.

Powder samples were prepared by grinding mixed oxides in the proper proportions in a mortar and pestle. A belt-type internally heated high-pressure apparatus (*3*) was used to effect synthesis. The samples were contained in platinum capsules, which also served as heaters.

No attempt was made to obtain oxygen analysis of the small samples at high pressure; however, previous experience with other oxide systems has indicated that oxygen is retained in the high-pressure capsules at elevated temperatures (*4*). Also the internal structure of the materials of this investigation indicated that the chemical composition of the final product was close to that of the original mixture.

Mixtures of $MoO_3$ and a metal monoxide were reacted at 60 kb and 900°C. The x-ray powder patterns of all the high-pressure samples were similar to those of wolframite. The powder patterns of some samples were quite diffuse. Annealing at 300°C in air generally resulted in somewhat sharper powder patterns.

The structure of the isostructural tungstates and high-pressure molybdates is monoclinic. However, the $\beta$ angle may differ by only minutes of arc from 90°. Because of ambiguity in indexing of higher order reflections, deviation of the $\beta$ angle from 90° can be definitely determined in powder patterns only by splitting in lower order reflections and most prominently by the (111) ($\bar{1}11$) splitting. This splitting was detected in only two high-pressure molybdates.

A comparison of the cell dimensions of the ambient-pressure tungstates as determined by Broch (*5*) and of the high-pressure molybdates is shown in Table 1. There may have been some undetected deviation from 90° in the $\beta$ angle for $MgMoO_4$, $FeMoO_4$, $CoMoO_4$, and $ZnMoO_4$. The cell dimensions of the wolframite-type tungstates and molybdates are very close as might be expected from the near equality of the radii of tungsten and molybdenum ions.

Table 1. Comparison of monoclinic unit cell dimensions in ambient-pressure tungstates (B) and high-pressure molybdates (H). The data on ambient pressure are Broch's (*5*).

| Compounds | a(Å) | b(Å) | c(Å) | $\beta$ |
|---|---|---|---|---|
| B, $MgWO_4$ | 4.68 | 5.66 | 4.92 | 89°40′ |
| H,$MgMoO_4$ | 4.66 | 5.64 | 4.86 | 90° |
| B, $MnWO_4$ | 4.84 | 5.76 | 4.97 | 89°7′ |
| H,$MnMoO_4$ | 4.82 | 5.75 | 4.96 | 89°10′ |
| B, $FeWO_4$ | 4.70 | 5.69 | 4.93 | 90° |
| H,$FeMoO_4$ | 4.62 | 5.64 | 4.90 | 90° |
| B, $CoWO_4$ | 4.66 | 5.69 | 4.98 | 90° |
| H,$CoMoO_4$ | 4.67 | 5.67 | 4.87 | 90° |
| B, $NiWO_4$ | 4.68 | 5.66 | 4.93 | 89°40′ |
| H,$NiMoO_4$ | 4.58 | 5.67 | 4.87 | 89°20′ |
| B, $ZnWO_4$ | 4.68 | 5.73 | 4.95 | 89°30′ |
| H,$ZnMoO_4$ | 4.71 | 5.74 | 4.90 | 90° |

To check the stability of the high pressure wolframite-type molybdates in air, samples were annealed at 300°C for 24 hours. There was no indication from the x-ray powder patterns of phase transformation. On holding in air at 500°C for 24 hours, partial phase transformation occurred. After 24 hours at 600°C transformation to the ambient pressure modification must have been nearly complete in all of the high pressure samples, since there were no visible reflections of the high pressure phases.

From the x-ray powder patterns, there appeared to be four crystal structure types in the ambient-pressure molybdates. The patterns of the transformed $CoMoO_4$ and $NiMoO_4$ were nearly identical and agreed with those found in ambient pressure compounds by Smith (*6*). The $MgMoO_4$ and $MnMoO_4$ patterns were also similar. This agrees with an observation by Brandt (*7*) who mentioned that ambient-pressure $MgMoO_4$ and $MnMoO_4$ were similar. The ambient-pressure compounds, $ZnMoO_4$ and $FeMoO_4$, each had a distinct powder pattern.

High-pressure modifications are necessarily denser than normally occurring compounds. From the Smith data (*6*) on $CoMoO_4$ and $NiMoO_4$ and from the high-pressure data shown in Table 1, the calculated densities of $CoMoO_4$ and $NiMoO_4$ are 4.79 and 4.94 g cm$^{-3}$, respectively, for the ambient pressure modifications and 5.61 and 5.74 g cm$^{-3}$ for the high-pressure wolframite-type modification. The wolframite-type $CoMoO_4$ and $NiMoO_4$ are 17.0 and 16.2 percent denser than the respective ambient pressure compounds.

Since the high-pressure molybdates all had the wolframite structure, it may be said that this is the structure characteristic of the small cation molybdates as well as for the tungstates. The structure of the ambient-pressure molybdate polymorphs depends on the divalent cation.

The failure to observe small cation molybdates isostructural with the wolframite-type tungstates has been cited as a problem, which could not be explained by the theories of modern crystal chemistry (*8*). This problem no longer exists since the wolframite-type molybdates have been synthesized. The reason for the requirement of pressure to produce wolframite-type molybdates is part of the common and largely unexplained problem of polymorphism. It is evident from this and other investigations that prophecies concerning possible high pressure polymorphs are justified. However, to explain why pressure is required for their production is not generally possible with present theories of crystal chemistry (*9*).

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#### References and Notes

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## Morphogenesis of Syncytiotrophoblast in vivo: An Autoradiographic Demonstration

Abstract. *In an in vivo autoradiographic study of immature primate trophoblast, tritiated thymidine was first found only in nuclei of cytotrophoblast but after 22 hours, labeled nuclei appeared in syncytiotrophoblast as well. Hence syncytiotrophoblast of the monkey appears to originate by differentiation of cytotrophoblast.*

The origin and function of syncytiotrophoblast has been a controversial subject (*1, 2*). Electron microscopic and immunohistochemical studies of benign and malignant trophoblast have strongly supported the concept that syncytiotrophoblast develops from cytotrophoblast as the differentiated form of trophoblast and has as a major function the synthesis of chorionic gonadotropin (*3, 4*). These conclusions would be proved if it could be shown that placental cytotrophoblast differentiated in vivo into syncytiotrophoblast.

Therefore an attempt was made to selectively label and follow the fate of cytotrophoblastic cells. Rhesus monkeys were selected because they have a chorio-allantoic type of placenta resembling closely that in man. Tritiated ($H^3$) thymidine, which is incorporated into newly synthesized deoxyribonucleic acid (DNA), was chosen for the label since, of the two trophoblastic cell types, mitosis has been demonstrated only in cytotrophoblast.

To ensure the use of immature developing trophoblast, early pregnancies were detected by assaying for chorionic gonadotropin, a hormone detectable in the serum of rhesus monkeys only between the 14th and 30th days of a 5- to 6-month gestation (*5*). The assay for chorionic gonadotropin was based on the appearance of ovarian hyperemia in weanling rats 3 to 18 hours after intraperitoneal injection of 1 ml of monkey serum. Pregnant monkeys were injected intravenously with 0.5 $\mu$c of $H^3$-thymidine per gram of body weight, and at intervals thereafter (Table 1) they were anesthetized with pentobarbital and either a hysterotomy with placental biopsy or hysterectomy was performed. All tissues were fixed in Bouin's fluid, embedded in paraffin, sectioned at 4 $\mu$, coated with Kodak AR 10 stripping film, and exposed at 4°C in plastic boxes containing Drierite. After sufficient exposure the slides were developed, stained with Harris' hematoxylin, differentiated in 0.2 percent HCl, and blued in 0.5 percent sodium acetate.

Immature chorionic villi were obtained from four monkeys at seven intervals and, as indicated in Table 1, in the first 12 hours all labeled nuclei appeared in cytotrophoblast; no labeled nuclei were seen in syncytiotrophoblast (Fig. 1). At 22 hours there were a few labeled nuclei in cells apparently intermediate in position between cytotrophoblast and syncytiotrophoblast, and a few more in outright syncytiotrophoblast. At 48 and 72 hours, labeled nuclei were found in both cytotrophoblast and syncytiotrophoblast in approximately equal numbers (Fig. 2). Since there was no evidence of independent synthesis of DNA in syncytiotrophoblast, which is in accord with the in vitro studies of Richart (*2*), the hypothesis that the syncytium increases by amitosis would appear to be untenable. Thus we concluded that syncytiotrophoblast is derived by differentiation of cytotrophoblast.

To substantiate this conclusion we studied immature villi and trophoblastic columns from these monkeys with an electron microscope. Our results (*6*) show that syncytiotrophoblast contains many dilated cysternae of endoplasmic reticulum, a feature of functioning differentiated cells (*7*), while cytotrophoblast contains many free ribosomes with few profiles of endoplasmic reticulum, a feature of rapidly dividing, undifferentiated cells (*8*). Cells midway in position between cytotrophoblast and syncytiotrophoblast (intermediate cells) possess features of both cell types. This suggests a developmental relationship between the undifferentiated and differentiated cells such as has been shown for other systems (*8*). Previous ultrastructural studies have shown similar intermediate cells in malignant human trophoblast (*3*).

Syncytiotrophoblast of the monkey seems to originate solely by differentiation from cytotrophoblast and, as the differentiated form of trophoblast, should be expected to perform the specialized functions of trophoblast. In

Table 1. Localization of nuclei in trophoblast labeled with $H^3$-thymidine. Time is given in hours after administration of $H^3$-thymidine.

| Time (hr) | Trophoblast | | |
|---|---|---|---|
| | Source | Cyto- | Syncytio- |
| 1 | Biopsy | + | − |
| 2½ | Biopsy | + | − |
| 4 | Hysterectomy | + | − |
| 12 | Hysterectomy | + | − |
| 22 | Hysterectomy | + | + |
| 48 | Biopsy | + | + |
| 72 | Hysterectomy | + | + |

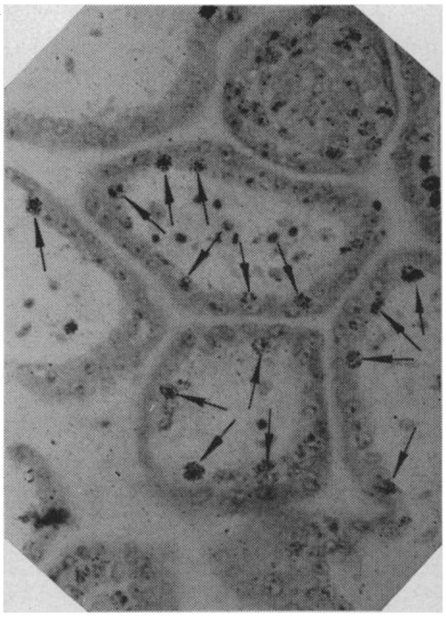

Fig. 1. Placental villi from a monkey 1 hour after it had received $H^3$-thymidine. Only cytotrophoblastic nuclei are labeled (see arrows). There are no labeled nuclei in syncytiotrophoblast.