# Metamunirite, a new anhydrous sodium metavanadate from San Miguel County, Colorado

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**Abstract**

Metamunirite, β-$NaVO_3$, is found in cavities in sandstone in San Miguel County, Colorado, occurring as fine, fibrous, colourless needles. X-ray powder and precession photographs show the crystals to be orthorhombic, space group *Pnma*, with $a = 14.134(7)$, $b = 3.648(2)$, $c = 5.357(2)$ Å. They are optically biaxial positive with $n_\alpha = 1.780(2)$ ($\|c$), $n_\beta = 1.800(2)$ ($\|a$), $n_\gamma \gg 1.85$ ($\|b$, fibre axis; positive elongation), $2V_z$ moderate. A crystal structure analysis, confirming the previously determined structure of β-$NaVO_3$, shows the presence of $(VO_3)_n$ chains made up of zig-zag $VO_5$ square pyramids. Metamunirite is probably formed by dehydration of munirite, $NaVO_3.2H_2O$.

KEYWORDS: metamunirite, vanadates, San Miguel County, Colorado, munirite.

## Introduction

THE most common vanadates occurring among the efflorescences within the weathered vanadium-bearing sandstones, such as those of the Colorado Plateau, are the orange-coloured decavanadates pascoite, hummerite, heumulite, and other unnamed decavanadate salts. In more alkaline environments the colourless metavanadates rossite and metarossite are more rarely found. Patrick E. Haynes, a mineral collector in Cortez, Colorado, has recently found excellent examples of rossite in the Burro mine, near Slick Rock, San Miguel County, Colorado. The mineral transforms to metarossite through loss of water ($CaV_2O_6.4H_2O \rightarrow CaV_2O_6.2H_2O$) in a few weeks' time in the open air. Mr. Haynes has also found in this setting, at the Burro mine and also at the nearby Deremo-Snyder mine, specimens showing clusters of radiating colourless needles up to 0.2 mm in length in cavities in sandstone, which have proved to be the orthorhombic form of sodium metavanadate, β-$NaVO_3$. This new mineral is described below, and named metamunirite in allusion to its probable relationship to munirite, $NaVO_3.2H_2O$. The name has been approved by the International Commission on New Minerals and New Mineral Names. The type material is so far extremely rare, and has been deposited with the Smithsonian Institution, Washington, D.C.

## Physical properties of metamunirite

The needle-like crystals, which sometimes are broadened into narrow laths, are extremely soft, friable and fibrous in character. They are scattered on the surface of a fracture cavity in sandstone in which some previously deposited clay filling is evident. The crystals are optically birefringent, showing positive elongation and parallel extinction. The indices of refraction of the natural fibres, measured in immersion oils, are about 1.78 normal to the fibre direction. The indices measured on a synthetic crystal (0.4 mm long) using a spindle stage are $n_\alpha = 1.780$, $n_\beta = 1.800$ (±0.002); $n_\gamma$ is much higher and was not measured. Optic angle $2V_z$ is estimated to be 30° to 40°. The orientation is $X = a$, $Y = c$, $Z = b$, with respect to the orthorhombic unit cell (see below). The average $n$ calculated from the composition and density by the Gladstone–Dale law (Mandarino, 1976) is 1.930. The density of metamunirite calculated from the unit cell volume containing $4NaVO_3$ is 2.926 g/cm$^3$; Perraud (1974) reported the density measured on his synthetic β-$NaVO_3$ to be 2.877 g/cm$^3$. The dominant crystal habit is {101}, with no clearly developed terminal faces. The easy splitting of the crystals into fibres probably occurs by perfect cleavage on this form, and on {001}. The crystals are readily soluble in water.

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### X-ray crystallography

X-ray powder data for metamunirite were obtained from natural fibres randomly oriented in a ball mount, using a Gandolfi camera and both Cu-$K\alpha$ and Cr-$K\alpha$ radiations. After eliminating lines due to quartz, the *d*-spacings were found to conform precisely to those recorded for $\beta$-$NaVO_3$ by Morris *et al.* (1981) (PDF No. 32-1198), as shown in Table 1. A fibre pattern was obtained on a bundle of natural crystals, which completely confirmed the indexing of *h0l* reflections as given in Table 1. Powder data have also been published for this phase by Lukács and Strusievici (1962), Feigelson *et al.* (1972), and Perraud (1974), all in substantial agreement with those given in Table 1. The similar data originally offered by Hanawalt *et al.* (1938) (PDF No. 1-246) were erroneously ascribed to $NaVO_3.H_2O$ (see description of dehydration phenomena below). Least-squares analysis of our Cr-$K\alpha$ powder data for the natural crystals yield the following unit cell parameters, shown below in comparison with the best published data:

| | This work | Morris *et al.* (1981) | Kato and Takayama (1984) |
|---|---|---|---|
| *a*, Å | 14.134(7) | 14.155(6) | 14.147(2) |
| *b*, Å | 3.648(2) | 3.6499(11) | 3.6496(6) |
| *c*, Å | 5.357(20 | 5.3625(15) | 5.364(1) |
| *V*, Å$^3$ | 276.3(3) | 277.1 | 276.96(9) |

This nonconventional cell orientation is retained here rather than the conventional cell of Morris *et al.* (1981) in order to facilitate the comparison of the *b* (fibre) axis with that of the monoclinic structure of munirite. The transformation from Morris *et al.* (1981) to this setting is (010/001/100).

A synthetic preparation of sodium metavanadate was crystallised from water solution at room temperature, yielding fibrous, radiating crystals entirely similar to the natural ones. A single crystal was selected from this preparation and used for precession photography and single-crystal intensity measurement by automatic diffractometry. The precession patterns showed a clearly resolved primitive orthorhombic lattice, but the spots were generally diffuse. The patterns confirm the unit cell and space group *Pnma* first defined by Lukács and Strusievici (1962) and later redetermined by Kato and Takayama (1984).

Using a modified Picker automatic single-crystal diffractometer with Mo$K\alpha$ radiation, 595 reflections with $2\theta < 40°$ were measured in the hemisphere. These were averaged to 154 independent observations, of which 71 had $I > 1.5\sigma(I)$. Weighted least-squares refinement of the structure parameters of Kato and Takayama (1984) led to the conventional reliability index $R_w = 0.070$ ($R = 0.18$) in isotropic thermal mode. The structure parameters obtained are in good agreement with those of Kato and Takayama (1984), and did not provide any improvement over their result.

### Chemical composition of metamunirite

An energy-dispersive X-ray test in the scanning electron microscope showed the presence of only sodium and vanadium in approximately equal amounts. Joseph Nelen of the Smithsonian Institution has kindly made a microprobe analysis of fibres from the Deremo-Snyder mine, mounted with epoxy resin on a glass slide. For this analysis an ARL SEMQ instrument was used with wavelength-dispersive technique: excitation voltage 15 kV; sample current 0.025 μa on brass; beam defocussed to 25 μm to reduced specimen heating; data processed with the MAGIC IV program. For 31 point determinations the following results were obtained (weight percent): $Na_2O$, 24.8; $V_2O_5$, 75.2. The theoretical values for $NaVO_3$ are 25.4 and 74.6 respectively. The standard deviation for both oxides is 0.4%. The sums were consistently deficient by 8 to 10%. No visible change in the specimen (boiling or poring) was observed such as would be expected from loss of water. The deficiency in the totals is attributed to the presence in the beam, in every test, of significant amounts of mounting medium, which could not be avoided because of the finely fibrous texture of the specimen. The slightly low value for Na may be caused by the volatility of Na relative to V. Nevertheless, the chemical composition is firmly established by the probe analysis and the X-ray diffraction studies described above.

### Crystal chemistry of metamunirite

The crystal structure analysis of metamunirite shows that the mineral phase is anhydrous, corresponding to the well-established polymorph of sodium metavanadate $\beta$-$NaVO_3$ (Fig. 1). From aqueous solutions, which presumably are the source of the natural metavanadates, Perraud (1974) has shown that the monoclinic phase $NaVO_3.2H_2O$ is stable below 34.6°C, but can exist metastably to higher temperatures. This phase constitutes the mineral munirite (Butt and Mahmood, 1983; Evans, 1988). Above 34.6 °C, according to Perraud, the anhydrous orthorhom-

Table 1. X-ray powder data for metamunirite and β-$NaVO_3$

| h k l | d(calc) min[1] | d(obs) min[2] | d(obs) syn[3] | I(rel) syn[3] | d(obs) std[4] | I(rel) std[4] | h k l |
|---|---|---|---|---|---|---|---|
| 2 0 0 | 7.07 | 7.07 | 7.03 | 28 | 7.09 | 11 | 2 0 0 |
| 1 0 1 | 5.01 | 5.05 | 5.03 | 100 | 5.01 | 100 | 1 0 1 |
| 2 0 1 | 4.269 | | | | 4.283 | 6 | 2 0 1 |
| 4 0 0 | 3.534 | 3.530 | 3.535 | 57 | 3.532 | 25 | 4 0 0 |
| 1 0 2 | 3.242 | 3.241 | 3 241 | 44 | 3.248 | 18 | 1 0 2 |
| 0 1 1 | 3.015 | 3.016 | 3.016 | 28 | 3.019 | 13 | 0 1 1 |
| 1 1 1 | 2.949 | 2.957 | 2.955 | 33 | 2.954 | 35 | 1 1 1 |
| 4 0 1 | 2.951 | | | | | | 4 0 1 |
| 0 0 2 | 2.679 | 2.685 | 2.689 | 11 | 2.683 | 12 | 0 0 2 |
| 1 0 2 | 2.632 | | | | 2.635 | 2 | 1 0 2 |
| 3 1 1 | 2.540 | 2.538 | 2.540 | 9 | 2.541 | 7 | 3 1 1 |
| 4 1 0 | 2.538 | | | | | | 4 1 0 |
| 2 0 2 | 2.505 | 2.499 | 2.508 | 4 | 2.506 | 5 | 2 0 2 |
| 5 0 1 | 2.501 | | | | | | 5 0 1 |
| 6 0 0 | 2.356 | | | | 2.360 | 2 | 6 0 0 |
| 3 0 2 | 2.329 | | | | 2.333 | 4 | 3 0 2 |
| 4 1 1 | 2.294 | 2.293 | 2.295 | 9 | 2.295 | 5 | 4 1 1 |
| 2 1 2 | 2.065 | 2.071 | 2.067 | 6 | 2.067 | 1 | 2 1 2 |
| 3 1 2 | 1.9628 | 1.9668 | 1.9642 | 13 | 1.965 | 5 | 3 1 2 |
| 7 0 1 | 1.8894 | 1.8938 | 1.8940 | 7 | 1.892 | 5 | 7 0 1 |
| 0 2 0 | 1.9242 | 1.8236 | 1.8242 | 19 | 1.824 | 6 | 0 2 0 |
| 1 0 3 | 1.7717 | 1.7767 | 1.7698 | 4 | 1.771 | 3 | 1 0 3 |
| 2 0 3 | 1.7313 | | | | 1.732 | 1 | 2 0 3 |
| 5 1 2 | 1.7159 | 1.7161 | 1.7171 | 4 | 1.716 | 5 | 5 1 2 |
| 8 0 1 | 1.6779 | | | | 1.679 | 2 | 8 0 1 |
| 4 2 0 | 1.6209 | 1.6204 | 1.6211 | 7 | | | 4 2 0 |
| 0 1 3 | 1.6039 | | 1.6051 | 9 | 1.6051 | 4 | 0 1 3 |
| 4 0 3 | 1.5938 | | | | | | 4 0 3 |
| 8 1 0 | 1.5902 | 1.5878 | 1.5892 | 5 | 1.5944 | 7 | 8 1 0 |
| 4 2 1 | 1.5515 | 1.5513 | 1.5500 | 2 | 1.5521 | 1 | 4 2 1 |
| 0 2 2 | 1.5077 | 1.5025 | | 4 | 1.5090 | 2 | 0 2 2 |
| 8 0 2 | 1.4749 | 1.4755 | 1.4703 | 1 | 1.4745 | 3 | 8 0 2 |
| 9 1 1 | 1.3929 | 1.3937 | 1.3926 | 5 | 1.3942 | 2 | 9 1 1 |
| 8 0 3 | 1.2560 | 1.2554 | | 3 | | | 8 0 3 |
| 4 2 3 | 1.2002 | 1.2002 | | 3 | | | 4 2 3 |
| 4 1 4 | 1.1845 | 1.1844 | | 2 | | | 4 1 4 |

Notes:

1. Calculated data for natural sample.
2. Metamunirite: Debye-Scherrer pattern, CrKα radiation; several quartz lines omitted.
3. Synthetic β-$NaVO_3$: Debye-Scherrer pattern, CrKα radiation; microdensitometer peak intensities.
4. Standard pattern (PDF 32-1198) for β-$NaVO_3$ (Morris et al., 1981).

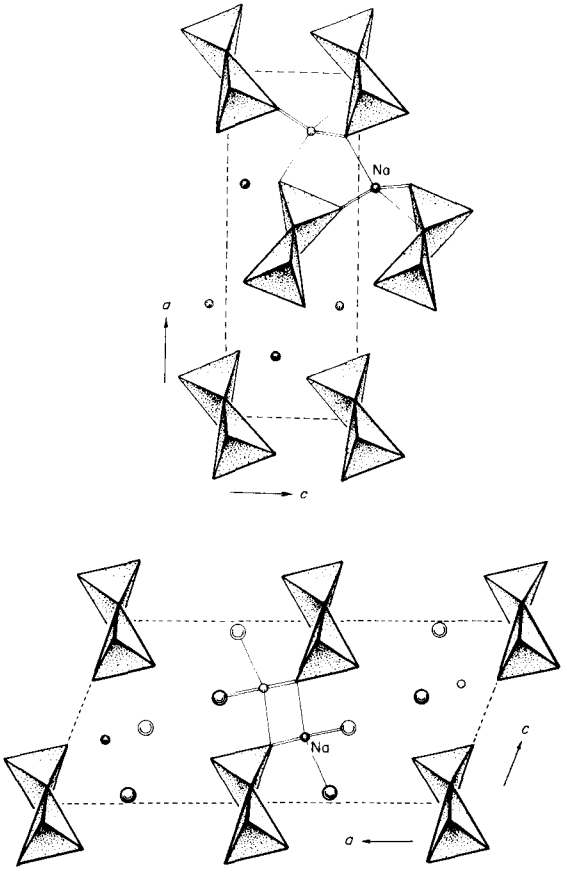


FIG. 1. Crystal structures of munirite in $P2_1/a$ according to Björnberg and Hedman, 1977 (top), and metamunirite in *Pnma* according to Kato and Takayama, 1984 (bottom). The end view of the $(VO_3)_n$ chains shows the zig-zag arrangement of the edge-shared $VO_5$ square pyramids. The distorted octahedral Na–O contacts are also indicated by fine lines.

bic phase β-$NaVO_3$ is formed stably from solution, but can form metastably below this temperature. Kato and Takayama (1984) have shown a close structural relationship of β-$NaVO_3$ to $NaVO_3.2H_2O$ (munirite; see Fig. 1). The latter tends to lose water in air, a process that can continue to the anhydrous state without serious disruption of the crystal structure. Kato and Takayama found evidence for the existence of an intermediate state, which would correspond to $NaVO_3.H_2O$. The metamurite crystals are often bounded by a broad (101) face (smeared optical signal) and a narrow (100) face (sharper signal). These faces are probably pseudomorphs after the forms (100) and (001) of munirite, respectively. The poor crystallinity of metamunirite (as shown by broadened Bragg reflections in both powder and precession photographs) probably results from its formation as a pseudomorph after a hydrated form such as munirite.

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