

which, combined with the microprobe analysis, gives a total of 99.9 percent. The X-ray powder pattern, indexed on Evans and Allmann's hexagonal cell yields cell dimensions  $a$  3.778 and  $c$  34.147 Å which are in close agreement with that of normal valleriite of  $a$  3.792 and  $c$  34.10 Å. The Noril'sk mineral appears to represent the end member of a series of "valleriite-type" minerals with the Mg-Al positions in the hydroxide layer occupied by Fe.

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TUNGSTENIAN WULFENITES, MINA SAN SAMUEL,  
CACHIYUYO DE LLAMPOS, CHILE

ALAN H. CLARK, *Department of Geological Sciences,  
Queen's University, Kingston, Ontario, Canada*

AND

RICHARD H. SILLITOE, *Instituto de Investigaciones  
Geológicas, Casilla 10465, Santiago de Chile.*

## ABSTRACT

Chemical analyses and cell dimensions are presented for a wulfenite and for two  $\text{Pb}(\text{Mo,W})\text{O}_4$  solid solutions from northern Chile. The latter are more molybdenum-rich than previously described "chillagites", and indicate that a complete series from wulfenite to stolzite may be represented in nature.

## INTRODUCTION

Whereas complete solid solution between tetragonal  $\text{PbMoO}_4$  and  $\text{PbWO}_4$  has been established by synthesis (Jaeger and Germs, 1921), few occurrences have been described of minerals with compositions intermediate between the natural analogues, wulfenite and stolzite. Of these, the "chillagite" from the Christmas Gift mine, Chillagoe, Queensland, appears to comprise a comparatively wide range of compositions from, approximately, wulfenite<sub>73</sub> to wulfenite<sub>51.5</sub> (Ullmann, 1913; Smith and Cannon, 1913; Mingaye, 1916), and remains the best-documented representative of the series. Williams (1966) found that three of sixty-four wulfenites from various localities contained  $>2$  percent tungsten, but did not provide complete analyses of these phases. Syritso and Chernik (1966) and Mexiner (1969) have provided less definitive analytical data for probable, molybdenum-rich members, while Easton and Moss (1966) report an analysis of a stolzite containing a small amount (0.8 weight percent) of  $\text{MoO}_3$ .

Published data (Smith and Cannon, 1913; Quodling and Cohen, 1938; Syritso and Chernik, 1966; Williams, 1966) for the cell dimensions of the naturally-occurring  $\text{Pb}(\text{Mo},\text{W})\text{O}_4$  solid solutions are scanty and, in part, inconsistent with the values found for the synthetic end-members by Sillén and Nylander (1943).

In the present note, we record the occurrence and compositions of wulfenite-stolzite solid solutions from a new locality.

## WULFENITE IN THE COPIAPÓ AREA, CHILE

Wulfenite is a widespread, though generally minor mineral in the oxidation zones of copper-polymetallic ore deposits in the Copiapó mining district of northern Chile (Sillitoe, 1969), almost invariably representing a transported phase. In most occurrences, it displays the bright, orange-yellow color and adamantine luster characteristic of the species, and forms tabular crystals up to 3 cm in diameter. Locally, however, markedly paler, straw-yellow colors are exhibited, suggestive (Palache, *et al.*, 1951) of the partial substitution of molybdenum by tungsten, or (S. A. Williams, in Hoffman, 1968) the existence of structural defects.

Material for analysis was collected from the dumps of the small San Samuel copper mine (Lat.  $27^\circ 4.4' \text{ S}$ .; Long.  $70^\circ 0.1' \text{ W}$ .), which works a body of brecciated and tourmalinized quartz porphyry. Molybdenite is a major constituent of the hypogene ore, which locally assays 2.5 percent Mo (Varlamoff, 1963), while scheelite occurs in smaller amounts. At this locality, the wulfenite forms unusually large, free-standing euhedra, overgrowing hydrothermally altered granodiorite along fracture planes, and ranging in color from medium orange-yellow to straw-

TABLE 1. ANALYSES AND CELL DIMENSIONS OF WULFENITE-STOLZITE SOLID SOLUTIONS, COPIAPÓ DISTRICT, CHILE

	PbMoO <sub>4</sub>	1 Mina Dulcinea	2 Mina San Samuel	3 Mina San Samuel	Chillagite, Queensland (Ullmann, 1913)	PbWO <sub>4</sub>
CaO		0.30	n.d. <sup>a</sup>	n.d.		
PbO	60.78	60.01	58.85	57.66	54.25	49.05
MoO <sub>3</sub>	39.22	39.03	32.70	28.65	17.52	
WO <sub>3</sub>		0.57	8.40	13.74	28.22	50.95
Total	100.00	99.91	99.95	100.05	99.99	100.00
a Å	5.424 <sup>b</sup>	5.430 <sup>c</sup>	5.428 <sup>c</sup>	5.431 <sup>c</sup>	5.44 <sup>d</sup>	5.448 <sup>b</sup>
c Å	12.076	12.074	12.064	12.060	12.10	12.016

<sup>a</sup> Not detected.

<sup>b</sup> Sillén & Nylander, 1943 ( $\pm 0.005$  Å).

<sup>c</sup>  $\pm 0.005$  Å.

<sup>d</sup> Converted from  $kx$  units (Quodling and Cohen, 1938).

yellow. The wulfenite crystals are, however, not detectably zoned in hand-specimen. They are largely flat, tabular on {001}, with edges dominated by {114}, {013}, and {011} (*cf.* Williams, 1966), but the paler individuals show a greater development of pyramidal faces, and several exhibit predominant steep, dipyramidal {111} forms (*cf.* Williams, 1966, Fig. 1D).

#### ANALYTICAL DATA

Two pale yellow dipyramidal crystals, of 2.5 and 2.7 cm in maximum dimensions, were separated under a binocular microscope, and analysed following the procedure developed by Easton and Moss (1966), which is specifically designed for the determination of coexisting molybdenum and tungsten. X-ray fluorescence scans were also made in search of Fe, V, Cr, As, Sb and other minor elements; these were, however, not detected. In addition, an orange-yellow, tabular crystal from the nearby Mina Dulcinea de Llampos was analysed. The analytical results are presented in Table 1.

The cell parameters of the three analysed specimens were determined in a Nonius Guinier-de Wolff quadruple-focussing camera, using Co-K $\alpha$  radiation, and silicon as an external standard (Table 1).

The analyses of the two San Samuel crystals satisfy the requirements of stoichiometric Pb(Mo,W)O<sub>4</sub> solid solutions, intermediate between wulfenite and stolzite. These phases are Ca-free, but the W-poor material

from Dulcinea contains minor amounts of that element. Palache *et al.* (1951) quote an analysis of a wulfenite from Chile with 6.88 percent CaO, and complete solid solution of the lead and calcium, scheelite-type tungstates and molybdates would be expected, although the few published analyses suggest that natural representatives may in general conform rather closely to the four bounding series.

The San Samuel phases are markedly poorer in tungsten than most previously described "chillagites," and indicate that a complete solid solution series from wulfenite to stolzite may indeed be represented in natural assemblages. The *a* and *c* parameters of the solid solutions display an essentially linear relation with those determined for synthetic  $\text{PbMoO}_4$  (*a* 5.424, *c* 12.076 Å) and  $\text{PbWO}_4$  (*a* 5.488, *c* 12.016 Å) by Sillén and Nylander (1943). The value of *c* = 12.10 Å [converted from the original kX units using Bragg's (1947) factor 1.00202] found for the type chillagite of Ullmann (~55.4 mole percent  $\text{PbMoO}_4$ ) by Quodling and Cohen (1938) may, therefore, be in error. The wulfenite from Mina Dulcinea has cell dimensions similar to those of synthetic  $\text{PbMoO}_4$ .

#### DISCUSSION

Neither the Dulcinea wulfenite nor the tungsten-bearing phases from Mina San Samuel are intimately associated with other oxidate lead minerals, and the Eh/pH conditions of their formation cannot therefore be estimated with confidence (*cf.* Williams, 1963, 1966). However, the observations summarized herein suggest that there may be a relationship between the tungsten content of wulfenite and the color and habit of this mineral in these deposits, the more tungsten-rich members displaying paler yellow colors and dipyramidal rather than tabular forms. This would be in conflict with the conclusions of Williams (1966), who proposed that the conditions of deposition, and not major or minor element concentrations, are the dominant controls on wulfenite habit; it is not known whether he examined specimens from northern Chile.

As Palache *et al.* (1951) suggest, the name chillagite is probably superfluous as a description of intermediate members of the wulfenite-stolzite series. However, because it has attained some currency, it might be retained for compositions between 20 and 80 mole percent  $\text{PbWO}_4$ , by analogy with the wolframite series.

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EICOSYL ALCOHOL: AN ORGANIC CONSTITUENT OF CALCITE  
FROM DEUTSCH-ALTENBURG, AUSTRIA

CHARLES J. KELLY, JR.,<sup>1</sup> *New England Institute,  
Ridgefield, Connecticut 06877.*

ABSTRACT

Analysis of red-tinted calcite from Deutsch-Altenburg, Austria, probably of Miocene age, failed to confirm the existence of a metal porphyrin compound as reported by H.

<sup>1</sup> Present address: Hubbard-Hall Chemical Co., 563 S. Leonard St., Waterbury, Connecticut 06708.