ACHALAITE, Fe²⁺TiNb₂O₈, A NEW MEMBER OF THE WODGINITE GROUP FROM THE LA CALANDRIA GRANITIC PEGMATITE, CÓRDOBA, ARGENTINA

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Abstract

Achalaite is a new mineral of the wodginite group from the La Calandria granitic pegmatite, Cañada del Puerto, Córdoba province, Argentina (31°25′S, 64°55′W). The mineral occurs as polygranular aggregates up to 1.5 cm across, included in albite $\pm$ quartz with exsolutions of Ta-rich rutile and intergrown with microlite-group minerals. Achalaite has a black color and streak, metallic luster, H = 5½, D_{calc} = 6.285 g/cm³, and appears to lack cleavage. In reflected light, it is light grey with a slightly violet tint in air, and light grey with an olive tint in oil. Its bireflectance in both air and oil is weak but noticeable. Pleochroism is not observed. With crossed polarizers anisotropy in air is weak, particularly noticeable along grain boundaries; in oil, it is medium with light to intermediate olive grey tint. Internal reflections have not been observed either in air or oil. Data on minimum and maximum reflectances for the COM wavelengths are [λ (nm): R_{air}, R_{oil} (%)]: 470: 16.89, 17.72 and 5.26, 5.76; 546: 16.49, 17.26 and 4.98, 5.32; 589: 16.34, 17.04 and 4.97, 5.26; 650: 16.23, 16.94 and 4.86, 5.19. Achalaite, indexed by analogy with wodginite, is monoclinic, space group $C2/c$, $Z = 4$. Refined unit-cell dimensions are a 9.422(4) Å, b 11.427(3) Å, c 5.120(1) Å, β 90.12° (4), V 551.2(3) Å³. The strongest five lines in the X-ray powder diffraction pattern are as follows (d [Å], I%, hkl): 3.630, 40, 220; 2.964, 100, $\overline{2}$21, 221; 2.493, 40, 041; 1.735, 40, $\overline{4}$02; 1.711, 50, $\overline{4}$41, 441. Eight electron microprobe analyses (WDS) gave the following mean composition: WO₃ 2.41, Nb₂O₅ 30.18, Ta₂O₅ 37.56, TiO₂ 6.90, ZrO₂ 0.88, SnO₂

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3.82, Fe_2O_3 4.35, FeO 7.54, MnO 5.14, CaO 0.02, UO_2 0.38, total 99.18 wt.%. The average empirical formula is: $(Fe^{2+}_{2.211}Mn_{1.524}Fe^{3+}_{0.226}U_{0.030}Ca_{0.009})_{\Sigma4.000}(Ti_{1.819}Fe^{3+}_{0.920}Ta_{0.579}Sn_{0.533}Zr_{0.150})_{\Sigma4.000}(Nb_{4.781}Ta_{3.000}W_{0.219})_{\Sigma8.000}O_{32}$, ideally $Fe^{2+}TiNb_2O_8$. Achalaite is the first member of the wodginite group with Nb dominant over Ta; it is genetically considered a post-magmatic phase. The name of achalaite (CNMNC – IMA 2013-103) derives from the Achala granite batholith, located in Córdoba, Argentina.

INTRODUCTION

Wodginite-group minerals are partially to almost fully ordered monoclinic oxides of (mainly) Nb, Ta, Sn, Ti, W, Zr, Fe, and Mn that occur mostly in granitic pegmatites. In some of these deposits, these oxides constitute an important ore of tantalum along with columbite-group and microlite-group minerals.

Wodginite was described as a new mineral species by Nickel *et al*. (1963a) from granitic pegmatites at Wodgina, Western Australia, Australia and the Tanco pegmatite, Bernic Lake, Manitoba, Canada. The structure of wodginite was initially refined by Grice (1973) and Graham & Thornber (1974). Ferguson *et al*. (1976) improved the earlier structural results and established the general formula as ABC_2O_8 with $Z = 4$ and space group $C2/c$, with all three cation sites in octahedral coordination. The A site is usually dominated by Mn, the B site by Sn, and the C site by Ta, but diadochy of Fe^{2+} at A, Ti, Ta, or Fe^{3+} at B, and Nb or W at C is widespread. Extensive substitutions of Fe for Mn and Ti for Sn were recognized soon after the discovery of wodginite (Vorma & Siivola 1967, Grice *et al*. 1972). New minerals based on these substitutions, all with Ta > Nb (*apfu*, atoms per formula unit), were subsequently described by Ercit *et al*. (1992a, b, c). All species currently accepted as part of the wodginite group (plus two not formally approved) are compiled in Table 1.

Achalaite is a member of a new subgroup with Nb dominant at the C site. In achalaite, Ti is dominant at the B site (even though Fe^{3+} and Ta are quite abundant cations at this position) and Fe^{2+} > Mn at the A site, being the Nb-rich counterpart of ferrotitanowodginite (Galliski *et al*. 1999). Achalaite was found in a granitic pegmatite located close to the western border of the Achala granite batholith, from which its name is derived, in the Sierras Grandes of Córdoba, Argentina. The mineral and its name were approved prior to publication by the CNMNC – IMA (IMA 2013-103). The type specimen is deposited in the collection of the Museo de Geología y Mineralogía "Dr. Alfred Stelzner" of the Universidad Nacional de Córdoba, Argentina, under the catalogue number 3279.

THE PARENT PEGMATITE

The granitic pegmatite from which the type specimen was collected, La Calandria, occurs at Cañada del Puerto, on the western slope of the Sierras Grandes de Córdoba, Córdoba province, Argentina. Many aplite and pegmatite dikes are particularly concentrated along the central-western margin of the Devonian composite Achala batholith (Lira & Kirschbaum 1990, Demange *et al*. 1996, Dorais *et al*. 1997, Galliski *et al*. 2016), intruded locally into the Lower Cambrian medium to high-grade metasedimentary country rock units of the San Carlos Metamorphic Complex (Gaido *et al*. 2000 and references therein).

TABLE 1. MINERALS BELONGING TO THE WODGINITE GROUP (SPACE GROUP *C*2/*c*)

Name	Composition	Unit-cell parameters				
		a (Å)	*b* (Å)	*c* (Å)	β (°)	*V* (Å³)
wodginite[1]	$MnSnTa_2O_8$	9.501(9)	11.453(2)	5.113(5)	91.00(6)	556.3(2)
ferrowodginite[2]	$Fe^{2+}SnTa_2O_8$	9.415(7)	11.442(6)	5.103(4)	90.8(1)	549.7(6)
titanowodginite[2]	$MnTiTa_2O_8$	9.466(2)	11.431(1)	5.126(1)	90.31(2)	554.6(1)
ferrotitanowodginite[3]	$Fe^{2+}TiTa_2O_8$	9.403(4)	11.384(3)	5.075(1)	90.55(2)	543.2(2)
lithiowodginite[4]	$LiTaTa_2O_8$	9.441	11.516	5.062	91.06	550.26
unnamed[2]	$Mn(Fe^{3+}_{0.5}Ta_{0.5})Ta_2O_8$					
unnamed[2]	$Fe^{2+}(Fe^{3+}_{0.5}Ta_{0.5})Ta_2O_8$					
achalaite[5]	$FeTiNb_2O_8$	9.422(4)	11.427(3)	5.120(1)	90.12(4)	551.2 (3)

All have been approved by the IMA, except for those labelled "unnamed". References: [1] Nickel *et al*. (1963a), [2] Ercit *et al*. (1992c), [3] Galliski *et al*. (1999), [4] Voloshin *et al*. (1990), [5] This paper.

At Cañada del Puerto (Fig. 1) some well zoned dikes have been described as topaz- and columbite-tantalite-bearing pegmatites (Gay & Lira 1984). These dikes, located at 31°25′21.7″S, 64°55′4.6″W (northern outcrops) and 31°25′32.5″S, 64°55′47.2″W (southern outcrops), make up the old surface mining works of the La Calandria mine. The dikes are considered to have been derived from the same batch of pegmatite melt. The name of the mining works is applied collectively to all of these dikes. Achalaite is described from the northern outcrops. In these outcrops, three subparallel pegmatite dikes are each separated by ~15–20 m; these dikes crop out discontinuously along a ~250 m strike length and are 0.2–1.5 m thick. The pegmatites are concordant with the schistosity of the regional metasedimentary units, i.e., with a strike of N25 to 28°E and a dip variable from 20 to 43°W. The metamorphic country rocks are mostly biotite-muscovite mylonitic gneisses ("augen gneiss") and subordinate metaquartzites and calc-silicate layers. Locally, the pegmatite dikes crosscut lens-shaped metagabbro bodies (Galliski et al. 2016). Contacts with the country rocks are sharp.

The pegmatites are well zoned, often symmetrically. A border zone, 1–2 cm thick, mostly composed of albite with subordinate quartz grains (~1 cm), grades into a coarser-grained (2–2.5 cm) zone, ~3 cm thick, made up of quartz, K-feldspar, albite, and some muscovite. The intermediate zone attains 0.15 to 1.3 m variable thickness and has a coarser grain size than the border zone. It is composed of K-feldspar, quartz, and albite, and includes as accessory minerals 1 to 3 cm sized topaz crystals (commonly replaced by yellowish green muscovite-$2M_1$), cm-sized nodules of triplite, some rounded grains of microlite-group minerals, and 1–2 cm aggregates of dark Nb-Ta oxides. In some parts of the pegmatites, a segmented quartz core is developed. The pegmatites of the La Calandria mine are genetically linked with some of the most evolved peribatholithic facies of the Achala granitic batholith and are possibly of Upper Devonian–Lower Carboniferous age.
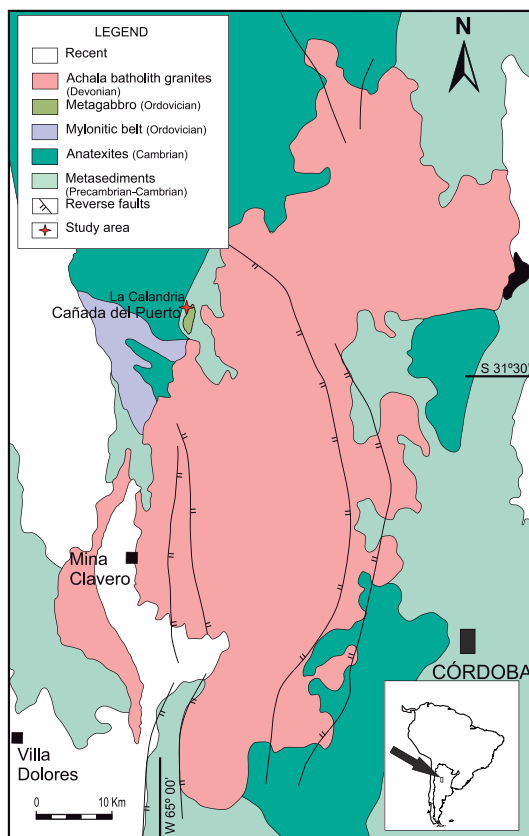

FIG. 1. Schematic map of the location and geology of the La Calandria pegmatite, Cañada del Puerto, Córdoba province, Argentina (modified from Gaido et al. 2000).

OCCURRENCE

The mineral forms black equidimensional polygranular masses up to 1.5 cm across, in association with Ta-rich rutile, pyrochlore-supergroup minerals, cassiterite, columbite-(Mn), ixiolite, and traces of bismuth, all included in quartz + albite + muscovite within the intermediate zone, close to the core of the pegmatite. Under the polarizing microscope and in backscattered electron images achalaite is intergrown with Ta-rich rutile and pyrochlore-supergroup minerals, all of them included in albite (Fig. 2). Exsolutions of microgranular Ta-rich rutile are very frequent.

The crystallization of achalaite is possibly due to subsolidus rearrangement of cations of a primary phase, likely an ixiolite-type structure, produced in an F-, H_2O-bearing environment during the cooling of the host pegmatite (Galliski et al. 2016).

PHYSICAL PROPERTIES

Achalaite is an opaque mineral with black color and streak, metallic luster, brittle tenacity, irregular fracture, H = 5½, and lack of fluorescence; cleavage was not observed. Microscopic inclusions of other phases precluded measurement of density; the calculated density based on the empirical formula is 6.285 g/cm³. The mineral is insoluble in HCl.
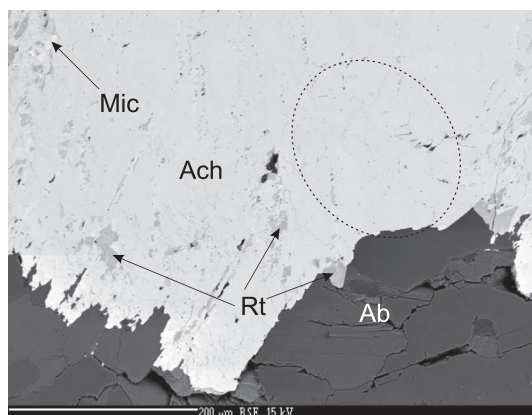
FIG. 2. Backscattered electron image of polished section CP-1-2 showing the different mineral phases. The light grey mineral is achalaite (Ach), the darker inclusions and exsolutions are Ta-rich rutile (Rt), the small white inclusions and exsolutions are fluornatromicrolite (Mic), and the dark mineral at the bottom of the image is albite (Ab). The dotted line shows the area from which the material for X-ray diffraction analysis was extracted.

TABLE 2. REFLECTANCE DATA FOR ACHALAITE IN AIR AND OIL

	in air		in oil	
λ (nm)	R_{min}	R_{max}	R_{min}	R_{max}
400	17.57	18.80	5.82	6.17
420	17.44	18.47	5.61	6.06
440	17.25	18.15	5.50	6.03
460	17.06	17.93	5.32	5.84
470	**16.89**	**17.72**	**5.26**	**5.76**
480	16.85	17.69	5.22	5.68
500	16.66	17.50	5.12	5.53
520	16.55	17.34	5.05	5.43
540	16.46	17.22	5.03	5.35
546	**16.49**	**17.26**	**4.98**	**5.32**
560	16.45	17.16	4.96	5.29
580	16.32	17.10	4.93	5.26
589	**16.34**	**17.04**	**4.97**	**5.26**
600	16.25	17.04	4.96	5.29
620	16.37	17.07	4.94	5.25
640	16.23	16.95	4.88	5.19
650	**16.23**	**16.94**	**4.86**	**5.19**
660	16.16	16.89	4.86	5.17
680	16.16	16.85	4.85	5.17
700	16.13	16.70	4.79	5.09

OPTICAL PROPERTIES

In plane polarized light achalaite is light grey with a slightly violet tint in air, and light grey with an olive tint in oil. Bireflectance in air and oil is weak but noticeable. Pleochroism is not recognized. The relative hardness of achalaite is: microlite < achalaite < Ta-rich rutile. With exactly crossed polarizers anisotropy in air is weak, especially recognizable along grain boundaries; in oil, it is medium, showing light to intermediate olive grey tints. Internal reflections have not been observed either in air or in oil. Two main patterns of undulose extinction are observed, one in patches and the other in bands.

The reflectance values were determined using a Leitz Orthoplan microscope attached to a Hamamatsu solid state mini-spectrometer *via* optical fiber, with dry and immersion 20× objectives (effective NA: 0.2 in air and oil) using SiC No. 878 as a standard; the oil conforms to the standard ISO 8036, with $n = 1.5180$. About 700 reflectance values for one spectrum were obtained and reduced to the required wavelength (400 to 700 nm) in steps of 20 nm, plus the four COM standard wavelengths. The obtained R1 and R2 values for air and oil are given in Table 2.

CHEMICAL COMPOSITION

Electron-microprobe analyses of the polished section of achalaite were carried out in wavelength-dispersive mode with a CAMECA SX100 instrument at the University of Manitoba. The accelerating voltage was 15 kV and the beam diameter was 2 μm. A sample current of 20 nA measured on a Faraday cup and a counting time of 20 s were used for each element; 10 s was used for the background. The standards used are as follows: $MnNb_2Ta_2O_9$ (Ta$M\alpha$), $CaNb_2O_6$ (Ca$K\alpha$), $FeNb_2O_6$ (Fe$K\alpha$), $MnNb_2O_6$ (Mn$K\alpha$, Nb$L\alpha$), rutile (Ti$K\alpha$), SnO_2 (Sn$L\alpha$), $CaWO_4$ (W$L\alpha$), UO_2 (U$M\beta$), and ZrO_2 (Zr$L\alpha$). The Na, K, Sr, Cs, Ba, Sb, Bi, and Pb contents were below the detection limit. Data were corrected using the PAP routine of Pouchou & Pichoir (1985).

The formula was calculated on the basis of 32 oxygen atoms and 16 cations, with Fe^{2+}/Fe^{3+} adjusted for electroneutrality. Since the pegmatite is Li-poor, this element was not considered to be present in achalaite. Possible vacancies at the A site were ignored as well. Following the practice of Ercit *et al.* (1992b), all of the W and Nb and part of the Ta were allocated to the C site. The elements Sn, Ti, Zr, and all of the Ta in excess of site C were allocated to the B site, as well as Fe^{3+} based on the determination by Turnock (1966) that it is localized at this site. All of the Mn, Ca, and U^{4+} (plus small amounts of remaining Fe^{3+}) were allocated to the A site. It should be noted that minerals with the wodginite structure are the only known natural phases with Ta-Nb order (Ercit *et al.* 1992b).

TABLE 3. ELECTRON-MICROPROBE COMPOSITIONS OF ACHALAITE (SAMPLE CP-01-2)

	B-07	B-08	B-09	B-10	B-12	B-13	B-16	B-25	Average	σ
wt.%										
WO_3	2.65	2.30	2.47	2.44	2.37	2.37	2.27	2.42	2.41	0.12
Ta_2O_5	38.22	37.62	37.45	37.65	36.98	37.27	37.68	37.58	37.56	0.36
Nb_2O_5	29.05	27.83	31.91	29.92	31.48	30.30	29.97	31.01	30.18	1.33
TiO_2	7.13	7.84	6.46	6.87	6.25	7.05	6.80	6.79	6.90	0.48
SnO_2	4.25	4.64	3.47	4.05	2.99	3.80	3.96	3.37	3.82	0.53
ZrO_2	0.95	0.93	0.77	0.96	0.78	0.93	0.90	0.81	0.88	0.08
Fe_2O_3	4.34	4.47	4.30	4.38	4.27	4.34	4.36	4.30	4.35	0.06
FeO	7.91	7.71	7.76	7.51	7.09	7.48	7.46	7.44	7.54	0.23
MnO	4.67	4.65	5.19	5.19	5.70	5.14	5.21	5.33	5.14	0.34
CaO	0.04	0.04	0.03	0.01	0.03	0.02	0.01	0.01	0.02	0.01
UO_2	0.33	0.53	0.33	0.36	0.37	0.37	0.31	0.47	0.38	0.08
Total	99.54	98.56	100.14	99.34	98.32	99.07	98.93	99.53	99.18	
apfu										
W	0.241	0.210	0.222	0.221	0.217	0.215	0.207	0.219	0.219	0.01
Nb	4.599	4.422	5.007	4.735	5.030	4.796	4.762	4.897	4.781	0.20
Ta	3.160	3.368	2.770	3.044	2.753	2.989	3.032	2.884	3.000	0.20
Σ C	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	
Ta	0.480	0.227	0.765	0.540	0.802	0.559	0.570	0.686	0.579	0.18
Ti	1.879	2.073	1.687	1.809	1.662	1.857	1.798	1.784	1.819	0.13
Zr	0.162	0.159	0.130	0.164	0.134	0.159	0.154	0.138	0.150	0.01
Sn	0.593	0.650	0.480	0.565	0.421	0.530	0.555	0.469	0.533	0.07
Fe^{3+}	0.886	0.890	0.938	0.922	0.980	0.894	0.923	0.922	0.920	0.03
Σ B	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	
Fe^{3+}	0.258	0.293	0.186	0.231	0.156	0.249	0.229	0.209	0.226	0.04
Fe^{2+}	2.316	2.267	2.251	2.198	2.097	2.190	2.192	2.174	2.211	0.07
Ca	0.015	0.015	0.011	0.004	0.011	0.008	0.004	0.004	0.009	0.00
Mn^{2+}	1.385	1.384	1.526	1.539	1.706	1.524	1.551	1.577	1.524	0.10
U^{4+}	0.026	0.041	0.025	0.028	0.029	0.029	0.024	0.037	0.030	0.01
Σ A	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	

Formulae expressed in atoms per formula unit (*apfu*), calculated based on 32 O atoms and 16 cations, with Fe^{2+}/Fe^{3+} adjusted for electroneutrality.

Analytical results and empirical chemical formulae are presented in Table 3. The average empirical formula ($n = 8$) is: $(Fe^{2+}_{2.211}Mn_{1.524}Fe^{3+}_{0.226}U_{0.030}Ca_{0.009})_{\Sigma 4.000}(Ti_{1.819}Fe^{3+}_{0.920}Ta_{0.579}Sn_{0.533}Zr_{0.150})_{\Sigma 4.000}(Nb_{4.781}Ta_{3.000}W_{0.219})_{\Sigma 8.000}O_{32}$. The ideal formula is $Fe^{2+}TiNb_2O_8$, which requires 63.65 wt.% Nb_2O_5, 19.14 wt.% TiO_2, and 17.21 wt.% FeO.

X-RAY DIFFRACTION

Wodginite-group minerals are monoclinic (space group $C2/c$). Ixiolite is the disordered equivalent of wodginite, and is orthorhombic but becomes monoclinic on heating. "Pseudo-ixiolite" (in the sense of Nickel *et al*. 1963b, but lacking valid species status) is actually a disordered columbite, and on heating it displays a well-ordered orthorhombic structure. Compared with disordered species belonging to the columbite group (orthorhombic, *Pbcn*), one of the most diagnostic features of the X-ray diffraction pattern of wodginite-group minerals is the order-driven splitting of the diffraction event located at about 30° (2θ). The single 111 peak of ixiolite (indexing based on *Pbcn* symmetry) becomes $\overline{2}21$ and 221 (indexing based on *C2/c* symmetry) for wodginite (see Ercit *et al*. 1992b).

Attempts to perform a single-crystal structural refinement of achalaite were hampered by the fact that this mineral occurs as finely polycrystalline aggregates, often with Ta-rich rutile exsolutions. Even in rutile-free samples, the separation of sets of reflections belonging to discrete crystals could not be performed due to the presence of multiple domains with different crystallographic orientations.

Since the material is chemically heterogeneous, and grades compositionally into other members of the wodginite group, special care was taken to perform the X-ray diffraction experiments on volumes whose
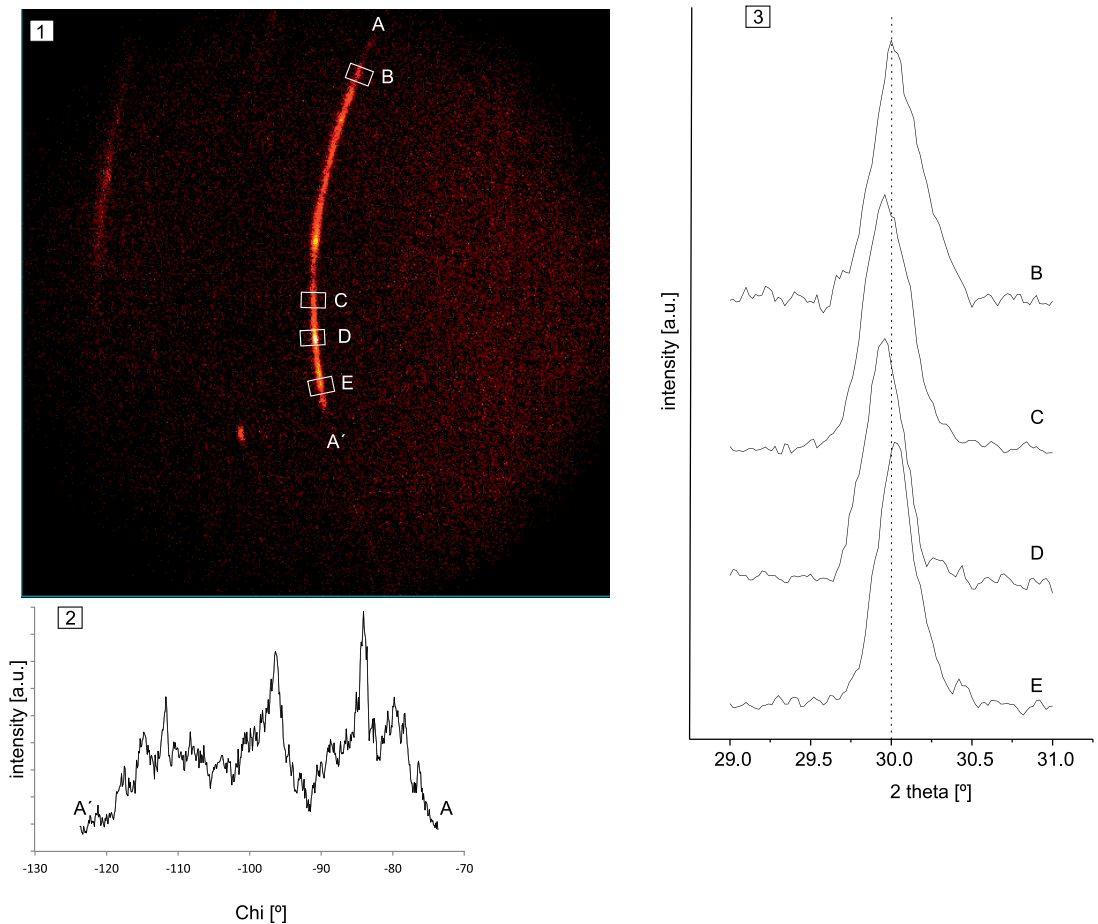
Fig. 3. (1) Frame measured using a GADDS instrument with Ni-filtered Cu$K\alpha$ radiation, operating at 40 kV and 20 nA, with a HISTAR detector of 1024 × 1024 pixels. Acquisition time was 3615 s. Contributions from many crystallites trace a discontinuous arc with some superimposed bright spots (such as in box D) corresponding to larger coherent domains. (2) This can also be seen in a plot along A–A' (arc located at about 30° 2θ). (3) Integrated profiles perpendicular to the arc (positions as indicated in Fig. 3-1), showing changes in both peak position and peak width. Peaks D or E are almost symmetrical, in contrast with peak B, which shows a gentler slope towards the high-angle side.

compositions correspond to achalaite proper. This led to rather small sample sizes.

A 0.75 mm piece of achalaite was removed from the polished microprobe section, then mounted on a single-crystal Si plate and examined using a General Area Detector Diffraction System (GADDS) at the Institut de Ciència de Materials de Barcelona. In this experiment, a single crystal would be expected to give sharp, discrete spots. By contrast, the obtained images of the stationary grain show discontinuous arcs (Fig. 3-1 and 3-2), indicating that the fragment is composed of multiple domains. Integrations of the image to give angle (2θ) *versus* intensity profiles were obtained at different places across the arc located at ≈30° (2θ)

(Fig. 3-3). Depending on the examined domain, peaks show variable full width at half height, and their profiles range from almost symmetric to slightly asymmetric (with gentler slope towards the high-angle side).

Peak broadening could be attributed to variable chemical composition or to the overlap of diffraction events from crystallites with variable structural states, where the $\bar{2}21$ and 221 peaks are incompletely resolved.

Inspection of Figure 3-3 suggests that the sample displays a variable degree of order, depending on the analyzed crystalline domain, where even the most asymmetric peak (labeled D) lacks the resolution of the $\bar{2}21$ and 221 peaks. Although experiments done
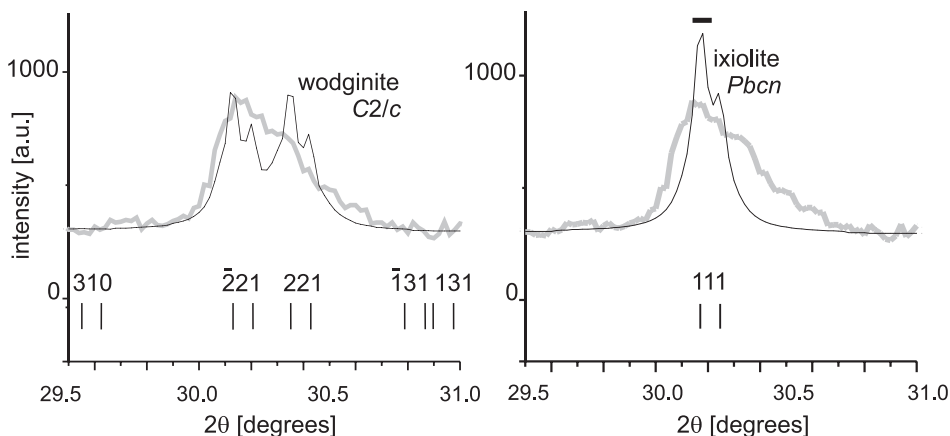
FIG. 4. Powder X-ray diffraction pattern of achalaite (grey), with superposed calculated patterns of wodginite (Ercit *et al*. 1992a) and ixiolite (Grice *et al*. 1976) (black) (see text for details). Note that the fit using the ixiolite structure cannot reproduce the shape of the peak, indicating the contribution of additional diffractions. Changes in Miller indices are due to different space groups. Pairs of bars with the same index indicate the position of $K\alpha_1$ and $K\alpha_2$ diffractions. The black bar above the ixiolite peak shows the expected range of peak positions due to changes in chemical composition.

with GADDS have intrinsically broad peak profiles, it can be seen that the shapes of some peaks approach symmetry, suggesting that some crystals show little (if any) ordering.

To date, the unit-cell dimensions of ixiolite cannot be accurately predicted by a given chemical composition because the influence of order/disorder has not been modeled. An approximation of unit-cell dimensions can be obtained using a model for ordered columbite, although it is known that disorder decreases the *a* parameter while increasing *c* (Ercit *et al*. 1995). Using the chemical compositions shown in Table 3 and the equations of Ercit *et al*. (1995) to account for the incorporation of variable amounts of Ti, Sn, and variable Ta/Nb and Fe/Mn ratios in the structure of columbite, we determined that the difference between the peak positions for the 111 diffraction event of ixiolite covers a range of about 0.04° (in 2θ, for Cu$K\alpha_1$ radiation). Even after allowing for some broadening due to the Cu$K\alpha_2$ line, the peaks should be narrower than those observed in the X-ray diffraction pattern of achalaite, thus leading to the conclusion that broadening cannot be attributed to chemical heterogeneity alone.

An X-ray powder diffractogram (Bragg-Brentano geometry) was obtained using a Philips X'Pert-PRO PW 3050 diffractometer housed at INFICQ University of Córdoba (Fig. 4). The diffractogram also shows considerable peak broadening that cannot be satisfactorily modeled using an orthorhombic unit cell. However, the introduction of a model corresponding to heated Fe^{2+}-rich wodginite (Ercit *et al*. 1992a), with

site occupancies modified to fit the empirical formula of achalaite, gave a reasonable match. By contrast, refinement of the XRPDP using the ixiolite model (taken from Grice *et al*. 1976) showed a poorer fit between calculated and observed peak positions and intensities. Unfortunately, because of the small sample size and the presence of abundant rutile, the intensities attributable to achalaite were too weak for a robust crystal structure refinement using the Rietveld method, and in any case the obtained values would just be weighted averages of the heterogeneous domains.

Additional X-ray diffraction data were obtained with a Debye-Scherrer camera at the Geological Survey of Canada. The analyzed area is shown in Figure 2. Peak positions were indexed based on the structure of wodginite (Table 4) and refined to give the following parameters: *a* 9.422(4), *b* 11.427(3), *c* 5.120(1) Å, β 90.12(4)°, *V* 551.2(3) Å^3.

Heating experiments were not done due to the abundance of inclusions which could lead to diffusion, which would give a phase that differs chemically from the original achalaite.

It is thus concluded that the material shows variable degrees of order at a very small scale, and that the symmetry of the (partially) ordered domains must be monoclinic, thus justifying the classification of achalaite as a member of the wodginite group. Peak broadening beyond that caused by chemical variability can be attributed to overlapping diffraction originating from multiple domains with different degrees of peak splitting, which cannot be resolved using conventional X-ray diffraction.

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR ACHALAITE

	$I_{(est.)}$	$d_{(meas.)}$ Å	$d_{(calc.)}$ Å	hkl
*	40	3.630	3.635	220
	100	2.964	2.966	$\bar{2}21$
			2.962	221
*	10	2.860	2.857	040
*	35	2.564	2.560	002
*	40	2.493	2.495	041
*	20	2.354	2.356	400
*	5	2.250	2.251	$\bar{2}02$
*	10	2.203	2.204	241
	30	2.092	2.095	$\bar{2}22$
			2.091	222
*	15	1.905	1.905	060
*	10	1.818	1.817	440
*	35	1.766	1.766	260
*	40	1.735	1.735	$\bar{4}02$
	50	1.711	1.714	$\bar{4}41$
			1.712	441
	30	1.545	1.546	$\bar{2}23$
			1.544	223
	3	1.524	1.528	062
	5	1.483	1.483	$\bar{4}42$
			1.481	442
*	15	1.465	1.465	043
	40	1.453	1.454	$\bar{2}62$
			1.454	550
			1.453	262
			1.453	$\bar{6}21$
			1.451	621

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni-filter (λ Cu$K\alpha$ = 1.54178 Å), not corrected for shrinkage and no internal standard; intensities estimated visually; indexed on a = 9.422(4), b = 11.427(3), c = 5.120(1) Å, β = 90.12(4)°; * lines used for unit-cell refinement.

Niobium-Dominant Members of the Wodginite Group — Other New Species and Favorable Precipitation Environments

In addition to achalaite, two other new members of the Nb-dominant subgroup were identified from the La Calandria pegmatite using electron microprobe analyses. Their endmember formulae are $Mn^{2+}(Fe^{3+}_{0.5}Ta^{5+}_{0.5})Nb_2O_8$ and $Fe^{2+}(Fe^{3+}_{0.5}Ta^{5+}_{0.5})Nb_2O_8$ (*cf.* Galliski *et al.* 2016, Table 1). Their formal descriptions will have to await the discovery of enough material, but show the potential of moderately oxidizing environments to stabilize other Nb-dominant phases of the wodginite group.

It is usually assumed that the ionic radii of Nb^{5+} and Ta^{5+} in octahedral coordination are the same, namely 0.64 Å (Shannon 1976). Thus, the geochemical

separation of these elements, which is one of the hallmarks of pegmatite crystallization, has been mostly attributed to processes based on the different solubility products of $MnNb_2O_6$ and $MnTa_2O_6$ in peraluminous pegmatitic melts (Linnen & Keppler 1997).

As mentioned above, wodginite is the only known mineral with a structure in which Nb and Ta are ordered. In spite of this, on crystallochemical grounds, *a priori*, there seems to be no reason to suspect that Nb-dominant equivalents of the recognized wodginite-group members would be unstable. Temperature also plays an important role, as experiments made in the Li_2O–Ta_2O_5 ($\pm$F) system show that above 695 °C $LiTaTa_2O_8$ adopts an orthorhombic (*Pnnm*) structure (Fallon *et al.* 1979, Hodeau *et al.* 1984), whereas lithiowodginite (*C2/c*) is stable below that temperature. Lithiotantite, $Li(Ta,Nb)_3O_8$, is very similar in chemical composition to lithiowodginite, and it is also monoclinic (but $P2_1/c$). It is isostructural with the only known crystal structure of $LiNbNb_2O_8$ (Lundberg 1971).

Tin (another species-defining metal in wodginite) also usually precipitates at a later stage than Nb-rich minerals in pegmatites, though it is not fractionated to the same extent as Li, and there are a number of reports of cassiterite paragenetically associated with columbite (*e.g.*, Tindle & Breaks 1998, Galliski *et al.* 2008, Rao *et al.* 2009, Martins *et al.* 2011). Moreover, there are a few cases where the usual trend of Ta and Mn enrichment is reversed, and deformed and recrystallized columbite-group minerals or cassiterite have lower Ta/(Ta + Nb) and Mn/(Mn + Fe) ratios in later units than they do in intermediate zones (*e.g.*, Novák *et al.* 2003, Rao *et al.* 2009, Chudik *et al.* 2011). It has been suggested that this reflects the high Nb content of early phases, either due to *in situ* replacement or due to the mobilization of Nb leached from other zones of the pegmatite (Černý *et al.* 1992). Such environments, with a Ta/Nb ratio $\leq$1 and the presence of Sn, would be appropriate places for precipitation of a Sn-dominant Nb oxide mineral.

Pegmatites with a low to moderate degree of fractionation (such as those belonging to the beryl-columbite-phosphate subclass) and with moderate F content are good candidates for the crystallization of $MnTiNb_2O_8$, as it has been shown that F promotes an increase in Mn/(Mn + Fe) ratio before appreciable Ta enrichment over Nb (Černý *et al.* 1986 and references therein).

REFERENCES

ČERNÝ, P., GOAD, B.E., HAWTHORNE, F.C., & CHAPMAN, R. (1986) Fractionation trends of the Nb- and Ta-bearing oxide minerals in the Greer Lake pegmatitic granite and its pegmatite aureole, southeastern Manitoba. *American Mineralogist* **71**, 501–517.

ČERNÝ, P., NOVÁK, M., & CHAPMAN, R. (1992) Effects of sillimanite-grade metamorphism and shearing on Nb-Ta oxide minerals in granitic pegmatites: Maršikov, northern Moravia, Czechoslovakia. *Canadian Mineralogist* **30**, 699–718.

CHUDIK, P., UHER, P., GADAS, P., ŠKODA, R., & PRŠEK, J. (2011) Niobium-tantalum oxide minerals in the Jezuitské Lesy granitic pegmatite, Bratislava Massif, Slovakia: Ta to Nb and Fe to Mn evolutionary trends in a narrow Be,Cs-rich and Li,B-poor dike. *Mineralogy and Petrology* **102**, 15–27.

DEMANGE, M., ÁLVAREZ, J.O., LÓPEZ, L., & ZARCO, J.J. (1996) The Achala batholith (Córdoba, Argentina): a composite intrusion made of five independent magmatic suites. Magmatic evolution and deuteric alteration. *Journal of South American Earth Sciences* **9(1–2)**, 11–25.

DORAIS, M.J., LIRA, R., CHEN, Y., & TINGEY, D. (1997) Origin of biotite-apatite-rich enclaves, Achala batholith, Argentina. *Contributions to Mineralogy and Petrology* **130**, 31–46.

ERCIT, T.S., HAWTHORNE, F.C., & ČERNÝ, P. (1992a) The wodginite group. I. Structural crystallography. *Canadian Mineralogist* **30**, 597–611.

ERCIT, T.S., ČERNÝ, P., HAWTHORNE, F.C., & McCAMMON, C.A. (1992b) The wodginite group. II. Crystal chemistry. *Canadian Mineralogist* **30**, 613–631.

ERCIT, T.S., ČERNÝ, P., & HAWTHORNE, F.C. (1992c) The wodginite group. III. Classification and new species. *Canadian Mineralogist* **30**, 633–638.

ERCIT, T.S., WISE, M.A., & ČERNÝ, P. (1995) Compositional and structural systematics of the columbite group. *American Mineralogist* **80**, 613–619.

FALLON, G.D., GATEHOUSE, B.M., ROTH, R.S., & ROTH, S.A. (1979) Crystal structures of some niobium and tantalum oxides, part VI. The structure of $H-LiTa_3O_8$. *Journal of Solid State Chemistry* **27**, 255–259.

FERGUSON, R.B., HAWTHORNE, F.C., & GRICE, J.D. (1976) The crystal structures of tantalite, ixiolite and wodginite from Bernic Lake, Manitoba. II. Wodginite. *Canadian Mineralogist* **14**, 550–560.

GAIDO, M.F., ZARCO, J.J., MIRÓ, R.C., SAPP, M., GAMBA, M.T., & LÓPEZ, H. (2000) *Hoja geológica 3166-30: Los Gigantes, provincia de Córdoba, 1:100000.* Servicio Geológico Minero Argentino, Instituto de Geología y Recursos Minerales, Buenos Aires, Boletín 299, 126 pp.

GALLISKI, M.A., ČERNÝ, P., MÁRQUEZ-ZAVALÍA, M.F., & CHAPMAN, R. (1999) Ferrotitanowodginite, $Fe^{2+}TiTa_2O_8$, a new mineral of the wodginite group from the San Elías pegmatite, San Luis, Argentina. *American Mineralogist* **84**, 773–777.

GALLISKI, M.A., MÁRQUEZ-ZAVALÍA, M.F., ČERNÝ, P., MARTÍNEZ, V., & CHAPMAN, R. (2008) The Ta-Nb-Sn-Ti oxide-mineral paragenesis at La Viquita, a spodumene-bearing rare-element granitic pegmatite from San Luis, Argentina. *Canadian Mineralogist* **47(2)**, 379–393.

GALLISKI, M.A., MÁRQUEZ-ZAVALÍA, M.F., ČERNÝ, P., LIRA, R., & FERREIRA, K. (2016) The complex Nb-Ta-Ti-Sn oxide intergrowths in La Calandria pegmatite, Cañada del Puerto, Córdoba, Argentina. *Canadian Mineralogist* **54** (this volume).

GAY, H.D. & LIRA, R. (1984) Presencia de topacio en la provincia de Córdoba. Yacencia, mineralogía y paragénesis en Tanti y Cañada del Puerto. *Revista de la Asociación Argentina de Mineralogía, Petrología y Sedimentología* **15(3–4)**, 62–66.

GRAHAM, J. & THORNBER, M.R. (1974) The crystal chemistry of complex niobium and tantalum oxides. II. Composition and structure of wodginite. *American Mineralogist* **59**, 1040–1044.

GRICE, J.D. (1973) *Crystal Structures of the Tantalum Oxide Minerals Tantalite and Wodginite, and of Millerite NiS.* Ph.D. Thesis, University of Manitoba, Winnipeg, Manitoba.

GRICE, J.D., ČERNÝ, P., & FERGUSON, R.B. (1972) The Tanco pegmatite at Bernic Lake, Manitoba. II. Wodginite, tantalite, pseudo-ixiolite and related minerals. *Canadian Mineralogist* **11**, 609–642.

GRICE, J.D., FERGUSON, R.B., & HAWTHORNE F.C. (1976) The crystal structures of tantalite, ixiolite and wodginite from

Bernic Lake, Manitoba I. Tantalite and ixiolite. *Canadian Mineralogist* **14**, 540–549.

Hodeau, J.L., Marezio, M., Santoro, A., & Roth, R.S. (1984) Neutron diffraction structure determination of the high-temperature form of lithium tritantalate, H-LiTa$_3$O$_8$. *Journal of Solid State Chemistry* **51**, 275–292.

Linnen, R.L. & Keppler, H. (1997) Columbite solubility in granitic melts: consequences for the enrichment and fractionation of Nb and Ta in the Earth's crust. *Contributions to Mineralogy and Petrology* **128**, 213–227.

Lira, R. & Kirschbaum, A.M. (1990) Geochemical evolution of granites from the Achala batholith of the Sierras Pampeanas, Argentina. *In* Plutonism from Antarctica to Alaska (S.M. Kay & C.W. Rapela, eds.). *Geological Society of America Special Paper* **241**, 67–76.

Lundberg, M. (1971) The crystal structure of LiNb$_3$O$_8$. *Acta Chemica Scandinavica* **25**, 3337–3346.

Martins, T., Lima, A., Simmons, W.B., Falster, A.U., & Noronha, F. (2011) Geochemical fractionation of Nb-Ta oxides in Li-bearing pegmatites from the Barroso-Alvão pegmatite field, northern Portugal. *Canadian Mineralogist* **49**, 777–791.

Nickel, E.H., Rowland, J.F., & McAdam, R.C. (1963a) Wodginite – a new tin-manganese tantalate from Wodgina, Australia and Bernic Lake, Manitoba. *Canadian Mineralogist* **7**, 390–402.

Nickel, E.H., Rowland, J.F., & McAdam, R.C. (1963b) Ixiolite – a columbite substructure. *American Mineralogist* **48**, 961–979.

Novák, M., Černý, P., & Uher, P. (2003) Extreme variation and apparent reversal of Nb-Ta fractionation in columbite-group minerals from the Scheibengraben beryl-columbite granitic pegmatite, Maršikov, Czech Republic. *European Journal of Mineralogy* **15**, 565–574.

Pouchou, J.L. & Pichoir, F. (1985) "PAP" (φρZ) correction procedure for improved quantitative microanalysis. *In* Microbeam Analysis (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California (104–106).

Rao, C., Wang, R.C., Hu, H., & Zhang, W.L. (2009) Complex internal textures in oxide minerals from the Nanping No. 31 dyke of granitic pegmatite, Fujian Province, southeastern China. *Canadian Mineralogist* **47**, 1195–1212.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica* **A32**, 751–767.

Tindle, A. & Breaks, F.W. (1998) Oxide minerals of the Separation Rapids rare-element granitic pegmatite group, northwestern Ontario. *Canadian Mineralogist* **36**, 609–635.

Turnock, A.C. (1966) Synthetic wodginite, tapiolite, and tantalite. *Canadian Mineralogist* **8**, 461–470.

Voloshin, A.V., Pakhomovskii, Y.A., & Bakhchisaraitsev, A.Y. (1990) Lithiowodginite - a new mineral of the wodginite group from granitic pegmatites in eastern Kazakhstan. *Mineralogicheskiy Zhurnal* **12**, 94–100.

Vorma, A. & Siivola, J. (1967) Sukulaite - Ta$_2$Sn$_2$O$_7$ - and wodginite as inclusions in cassiterite in the granite pegmatite in Sukula, Tammela in SW Finland. *Comptes Rendus de la Société Géologique de Finlande* **39**, 173.