Ecandrewsite, the zinc analogue of ilmenite, from Little Broken Hill, New South Wales, Australia, and the San Valentin Mine, Sierra de Cartegena, Spain

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Abstract

Ecandrewsite, the zinc analogue of ilmenite, is a new mineral which was first described from the Broken Hill lode in 1970 and discovered subsequently in ores from Little Broken Hill (New South Wales) and the San Valentin Mine, Spain. The name 'ecandrewsite' was used in a partial description of the mineral in 'Minerals of Broken Hill' (1982), thereby establishing the Little Broken Hill locality, specifically the Melbourne Rockwell Mine, as the type locality. Microprobe analysis of ecandrewsite from the type locality gave ZnO 30.42 (wt.%), FeO (total Fe) 11.37, MnO 7.64, TiO_2 50.12, total 99.6%, yielding an empirical formula of $(Zn_{0.59}Fe_{0.24}Mn_{0.17})_{1.00}Ti_{0.99}O_3$ based on 3 oxygen atoms. All compositions from Little Broken Hill and the San Valentin Mine are ferroan manganoan ecandrewsite. The strongest lines in the X-ray powder diffraction data are (d in Å, ($hkil$), I/I_o):2.746, ($10\bar{1}4$), 100; 2.545, ($11\bar{2}0$), 80; 1.867, ($02\bar{2}4$), 40; 3.734, ($01\bar{1}2$), 30; 1.470, (3030), 30; 1.723, ($11\bar{2}6$), 25. Ecandrewsite is hexagonal, space group $R\bar{3}$ assigned from a structural study, with $a = 5.090(1)$, $c = 14.036(2)$Å, V = 314.6(3)Å^3, Z = 6, D(calc.) = 4.99. The mineral is opaque, dark brown to black with a similar streak, and a submetallic lustre. In plane polarized light the reflection colour is greyish white with a pinkish tinge. Reflection pleochroism is weak, but anisotropism is strong with colours from greenish grey to dark brownish grey. Reflectance data in air between 470 and 650 nm are given. At the type locality, ecandrewsite forms disseminated tabular euhedral grains up to 250 × 50 μm, in quartz-rich metasediments. Associated minerals include almandine–spessartine, ferroan gahnite and rutile. The name is for E. C. Andrews, pioneering geologist in the Broken Hill region of New South Wales. Type material consisting of one grain is preserved in the Museum of Victoria (M35700). The mineral and name were approved by the IMA Commission on New Minerals and Mineral Names in 1979.

KEYWORDS: ecandrewsite, new mineral, metasediments, Melbourne Rockwell Mine, Little Broken Hill, Broken Hill, New South Wales, San Valentin Mine, Spain.

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Introduction

THE zinc analogue of ilmenite was first reported from the North Mine at Broken Hill, New South Wales, by Brown *et al.* (1970) but was neither described in full nor named. Several years later the mineral was discovered in quartz-rich metasediments at the Melbourne Rockwell Mine at Little Broken Hill, 13 km southeast of the main Broken Hill deposit in western New South Wales. The mineral was fully characterized in a submission by V. J. Wall and M. A. Etheridge to the IMA Commission on New Minerals and Mineral Names (CNMMN) in 1979. Both the mineral and the name, ecandrewsite, were approved by the CNMMN. However, apart from a brief summary of the occurrence and the main features of the Little Broken Hill mineral by Birch *et al.* (1982), based on information supplied by V. J. Wall, a full description has never been published.

TABLE 1. Electron microprobe analyses for ecandrewsite

Wt. %	1	2	3	4
TiO_2	50.85	52.45	51.7	50.12
FeO	8.8	12.05	13.65	11.37
MnO	4.4	6.15	5.0	7.64
ZnO	35.05	29.35	28.5	30.42
Total	99.1	100.0	98.85	99.55

Formulae on basis of 3 oxygen atoms

1. $(Zn_{0.69}Fe_{0.19}Mn_{0.10})Ti_{1.01}O_3$ (San Valentin Mine)
2. $(Zn_{0.56}Fe_{0.26}Mn_{0.13})Ti_{1.02}O_3$ (San Valentin Mine)
3. $(Zn_{0.55}Fe_{0.30}Mn_{0.11})Ti_{1.03}O_3$ (San Valentin Mine)
4. $(Zn_{0.59}Fe_{0.24}Mn_{0.17})Ti_{0.99}O_3$ (Little Broken Hill)

In 1977, C. Kieft, E. A. J. Burke and I. S. Oen identified the zinc analogue of ilmenite in ore specimens from the San Valentin Mine, La Union district, Sierra de Cartegena, Spain. These authors submitted a complete descrition, with a name, to the CNMMN, early in 1979, only to be informed by the Chairman at that time, Dr A. Kato, that the ecandrewsite submission had been received one month earlier and therefore had priority. As a result, Kieft *et al.* withdrew their proposal and awaited publication of the ecandrewsite description. This did not appear within the two-year limit set by the CNMMN.

In 1984, one of the authors (W.D.B.) was approached by the Chairman of the CNMMN, Dr J. A. Mandarino, with a request to endeavour to achieve publication of the full description of ecandrewsite. This paper is the result of those attempts and presents all available data for the three known occurrences.

The name is for E. C. Andrews, New South Wales Government Geologist (1870–1948), whose superb mapping of the Broken Hill region enabled many of its complexities to be understood. The type locality is the Melbourne Rockwell Mine in the Little Broken Hill field (Williams, 1967), 13 km southeast of the city of Broken Hill, New South Wales. A single grain of this type material is preserved in the collection of the Museum of Victoria (M35700). The whereabouts of specimens described originally from the North Mine at Broken Hill (Brown *et al.*, 1970) are unknown (Riley, pers. comm., 1984). Specimens of the mineral from the San Valentin occurrence are deposited in the collections of the Free University, Amsterdam, The Netherlands.

Occurrence

Ecandrewsite was first discovered in flotation residues containing cerussite, coronadite, gahnite and smithsonite, the source material being oxidized lead ore containing galena, coronadite, sphalerite and gahnite, from the vicinity of the No. 1 Shaft in the North Mine at Broken Hill (Brown *et al.*, 1970). The mineral has not been located *in situ* in the main Broken Hill lode. However, as zincian ilmenite (Zn < Fe, Mn) is quite common in the 'lode quartzites' and iron-rich amphibolites at Broken Hill and has also been found in patches of coarse ore in the Zinc Corporation Mine (Plimer and Ashley, 1978), it is possible that ecandrewsite is more widespread. The two minerals can only reliably be distinguished by chemical analysis.

At the type locality, the Melbourne Rockwell Mine, ecandrewsite forms euhedral grains up to 250 by 50 μm with tabular habit, disseminated in quartz-rich metasediments of amphibolite–granulite facies. It coexists with almandine–spessartine, ferroan gahnite and rutile. Associated amphibolites contain zincian ilmenite.

In the San Valentin lead/zinc mine, ecandrewsite occurs in primary oxide–sulphate–carbonate ores as intergrowths with zincian ilmenite up to 50 μm across (Oen *et al.*, 1975).

Physical and optical properties

The physical and optical properties of ecandrewsite from both the type locality and the San Valentin Mine are virtually identical to those of ilmenite. The mineral is dark brown to black with a submetallic lustre and dark brown to black

TABLE 2. X-ray powder diffraction data for ecandrewsite

1			2		3	
d	I	hkil	d	I	d	I
3.734	28	$01\bar{1}2$	3.69	2	3.7	W
					3.3	W
2.746	100	$10\bar{1}4$	2.73	10	2.72	VS
2.545	77	$11\bar{2}0$	2.53	9	2.52	S
2.236	21	$11\bar{2}3$	2.23	6	2.20	M
1.867	37	$02\bar{2}4$	1.87	4	1.86	MW
1.723	26	$11\bar{2}6$	1.71	7	1.71	M
1.631	10	$01\bar{1}8$			1.62	W
1.505	18	$21\bar{3}4$	1.502	2	1.50	W
1.470	31	$30\bar{3}0$	1.469	2	1.46	W
					1.40	VW
					1.36	VW
1.338	11	1.0.1.10			1.33	VW
					1.15	W

1. Little Broken Hill (calculated from single crystal data)
2. San Valentin Mine (Fe-K radiation, 57.54mm camera)
3. North Mine (Cobalt radiation, 57.3mm camera, data not indexed) Brown et al, 1970)

streak. In reflected light, ecandrewsite is greyish white with a pinkish tinge. Reflection pleochroism is weak in air but the mineral is strongly anisotropic between crossed polars, with colours changing from greenish grey to dark brownish grey. Neither cleavage nor twinning is observed in polished section. Direct measurement of reflectance in air on a grain of ecandrewsite from the type locality, using a Vickers digital microphotometer and a silicon carbide standard, gave the following data:

470 nm: R_o = 19.2–19.9, R'_e = 17.2–17.7
546 nm: R_o = 19.0–19.7, R'_e = 17.2–17.6
589 nm: R_o = 18.9–19.6, R'_e = 17.0–17.6
650 nm: R_o = 18.7–19.2, R'_e = 16.8–17.5

Neither reflectance nor microhardness were measured on the San Valentin Mine ecandrewsite due to the small grain size. However, grains from the type locality have Vickers microhardness of 500–600 kg/mm (load = 100 g).

The specific gravity could not be measured due to the small grain size in both occurrences, but the calculated value is in the range 4.98 (San Valentin Mine) to 4.99 (type locality).

Chemistry

Ecandrewsite from the type locality was analysed with a JEOL JXA5/A electron microprobe at 20 kV using synthetic ZnS (for Zn), natural rhodonite (Mn), rutile (Ti) and hematite (Fe) as standards. Ilmenite, rhodonite and zinc metal were used as standards for electron microprobe analysis (Cambridge Mark 9 instrument, 20 kV) of the San Valentin Mine mineral. Results are given in Table 1. Zinc contents are variable, with the maximum recorded being 37 wt.% for the North Mine mineral (Brown *et al.*, 1970). The empirical formulae, based on 3 oxygen atoms, are also shown in Table 1. Taking the ideal formula for ecandrewsite as $ZnTiO_3$, then all compositions obtained are ferroan manganoan ecandrewsite. Unpublished data for the Little Broken Hill and San Valentin Mine occurrences suggest that there is continuity of zinc substitution between ilmenite and ecandrewsite.

X-ray diffraction and structure

Complete X-ray diffraction data for ecandrewsite are listed in Table 2. For the San Valentin Mine mineral, data correspond to an hexagonal cell with a = 5.09, c = 13.95 Å, V = 312.99 Å^3, Z = 6, or to a rhombohedral cell with a 5.50 Å, α = 55°07′, Z = 2. The strongest lines in the X-ray powder diffraction pattern for ecandrewsite from the type locality are listed in Table 2. These were calculated from X-ray single crystal measurements carried out on the type specimen by Gatehouse and Nesbit (1978). Unit cell dimensions from 14 measurements of 22 reflections with 7.4 $\leqslant \theta \leqslant$ 14.0° resulted in mean values of a = 5.090(1) and c = 14.036(2)Å, corresponding to a unit cell volume of 314.6 Å^3 for Z = 6. One hundred and sixty six reflections ($I \leqslant 3\delta(I)$) were countermeasured using a Philips PW1100 single

crystal diffractometer with Mo–Kα radiation (0.7107 Å). Space group $R\bar{3}$ resulted from successful refinement, for which $R = 0.027$ and $R_w = 0.030$.

Crystal chemical data for both the San Valentin and Little Broken Hill specimens are in close agreement with those of synthetic $ZnTiO_3$ (hexagonal, $R\bar{3}$, $a = 5.07833(3)$, $c = 13.927(1)$Å, $Z = 6$; PDF26-1500) and confirm ecandrewsite is isostructural with ilmenite.

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