WÖHLERITE: CHEMICAL COMPOSITION, CATHODOLUMINESCENCE AND ENVIRONMENT OF CRYSTALLIZATION

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ABSTRACT

The occurrence of the niobium-bearing mineral *wöhlerite* $NaCa_2(Zr,Nb)Si_2O_7(O,OH,F)_2$ has been extended from agpaitic nepheline syenite to ijolite–pyroxenite, carbonatite and silicocarbonatite. Wöhlerite generally can be identified by its diagnostic blue-green cathodoluminescence (CL), which allows it to be identified in rocks where it has escaped recognition by investigators using routine petrographic techniques. CL emission spectra for wöhlerite from different localities are essentially the same, consisting of a band at *ca*. 500 nm, which is attributed to Mn^{2+} activation, and a broad sweeping band that covers the entire visible spectrum and is suspected to be intrinsic. Niocalite and hiortdahlite, two minerals that are sometimes compared chemically and crystallographically with wöhlerite, show distinctly different CL emission spectra because of trivalent *REE* activators. Results of electron-microprobe analyses for wöhlerite from six localities show a range for Nb_2O_5 concentration between 12 and 16 wt.%. The analytical data support the structural formula reported by Mellini & Merlino (1979). The inverse relationship of Nb^{5+} and F^{1-} suggests a coupled substitution with Ti^{4+} and O^{2-}, as described by Mellini & Merlino. The intensity of CL of wöhlerite is inversely related to the iron content; wöhlerite containing more than 1% FeO shows no CL. Wöhlerite from Prairie Lake, Ontario shows a zoned CL and a zoning of FeO. In carbonatite exploration programs, Nb assays commonly are assumed to represent only pyrochlore mineralization, but in the Prairie Lake complex, some carbonatites and other alkaline rocks may derive their Nb content almost exclusively from wöhlerite.

Keywords: wöhlerite, carbonatite, alkaline rocks, cathodoluminescence, chemical analyses, CL, emission spectra, niobium.

SOMMAIRE

La wöhlerite, $NaCa_2(Zr,Nb)Si_2O_7(O,OH,F)_2$, minéral accessoire riche en niobium, est présent non seulement dans les syénites néphéliniques agpaïtiques, mais aussi dans les ijolites–pyroxénites, carbonatites et silicocarbonatites. Sa couleur diagnostique bleu-vert en cathodoluminescence (CL) en assure l'identification, même où elle avait échapé à l'attention des chercheurs se fiant aux méthodes pétrographiques ordinaires. Les spectres d'émission CL de la wöhlerite provenant de différents milieux se ressemblent tous; ils contiennent une bande à environ 500 nm qui serait due à une activation par le Mn^{2+}, et une bande floue qui couvre le domaine visible du spectre au complet, et qui serait intrinsèque. La niocalite et la hiortdahlite, qui sont souvent comparées chimiquement et cristallographiquement à la wöhlerite, possèdent un spectre d'émission distinct à cause d'une activation par des terres rares trivalentes. Les données obtenues à la microsonde électronique pour des échantillons de six complexes révèlent entre 12 et 16% de Nb_2O_5. Ces données confirment la formule structurale de Mellini et Merlino (1979). La relation inverse entre le Nb^{5+} et le F^{1-} fait penser qu'il y a une substitution couplée impliquant Ti^{4+} et O^{2-}, telle que décrite par Mellini et Merlino. L'intensité de la cathodoluminescence de la wöhlerite est inversement liée à sa teneur en fer; les échantillons qui contiennent plus de 1% de FeO ne montrent pas d'effet CL. La wöhlerite du lac Prairie, en Ontario, qui montre une zonation de l'effet CL, est effectivement zoné dans sa teneur en fer. Dans les programmes d'exploration des complexes de carbonatite, les teneurs en Nb sont souvent entièrement attribuées au pyrochlore, mais dans certaines unités de carbonatite et de roches alcalines du massif du lac Prairie, le niobium serait presque exclusivement sous forme de wöhlerite.

(Traduit par la Rédaction)

Mots-clés: wöhlerite, carbonatite, roches alcalines, cathodoluminescence, composition chimique, CL, spectre d'émission, niobium.

INTRODUCTION

Wöhlerite is generally considered to be a rare mineral and to occur in a restricted geological environment (Vlasov 1966). It is most often reported in nepheline syenite, both agpaitic and miaskitic, and their pegmatite derivatives. It is also known to occur in fenites associated with alkaline massifs. Vlasov (1966) discussed occurrences of wöhlerite in basalt, trachyte and phonolite from Tasmania and Victoria, Australia, but no references or details of the occurrences were given. According to Kapustin (1980), wöhlerite is not observed in carbonatites.

In this study, we report the presence of wöhlerite in carbonatite, silicocarbonatite, melteigite, ijolite, urtite, pyroxenite and malignite, indicating that the mineral has a more widespread distribution than has
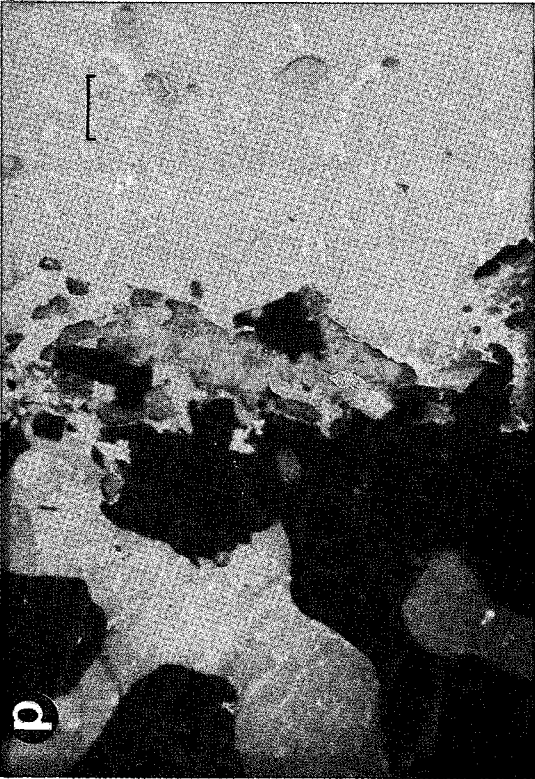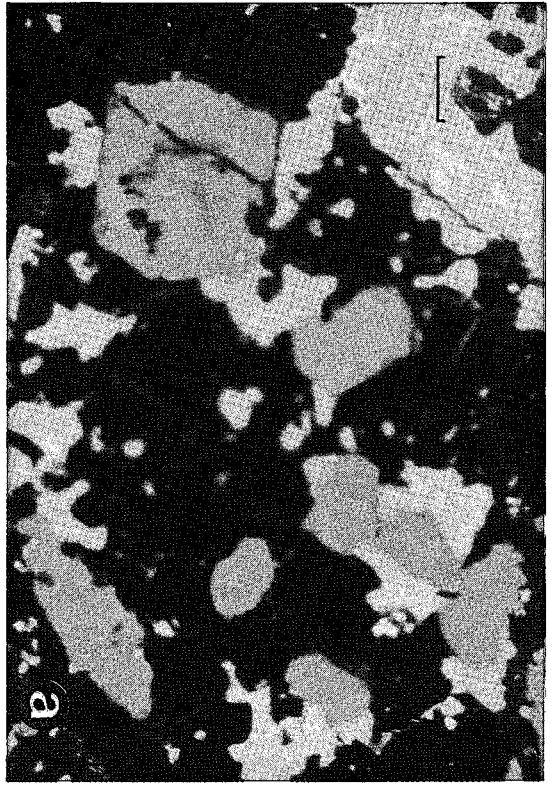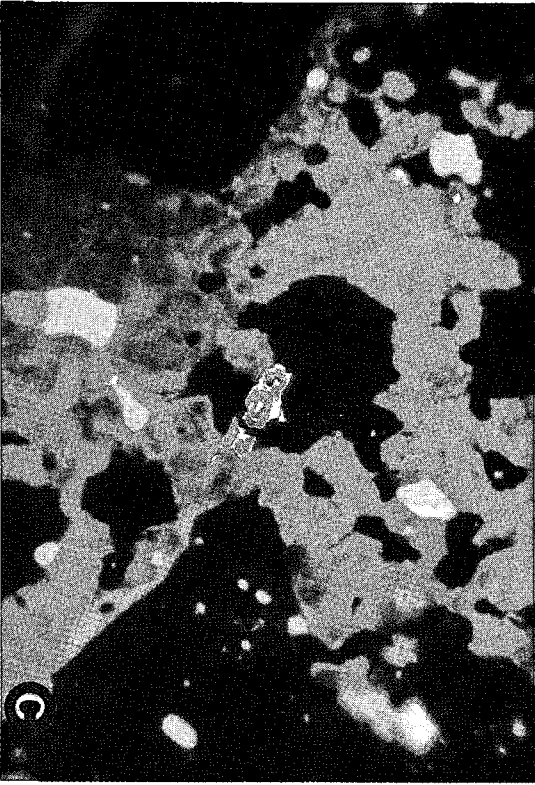
been previously reported. Wöhlerite commonly is found with other niobium-bearing minerals including pyrochlore, betafite, latrappite, niobian perovskite, and niobian zirconolite. The identification of wöhlerite in carbonatite and associated alkaline rocks is of importance if niobium partition coefficients are being evaluated for specific rocks. Furthermore, in exploration programs that focus on carbonatite, niobium assays are generally assumed to represent pyrochlore mineralization, but at least in the Prairie Lake carbonatite in Ontario, the malignites and ijolite–pyroxenite rock types may derive their niobium content almost exclusively from wöhlerite mineralization.

Wöhlerite occurs as elongate prisms that may be several centimeters long; it can be recognized with relative ease at the type locality at Langesundfjord, Brevik, Norway. Most commonly, wöhlerite assumes microscopic dimensions and is intimately associated with other minerals, obscuring its identification. In many cases, however, wöhlerite can readily be differentiated from other minerals by its cathodoluminescence (CL), which consists of a diagnostic blue-green coloration.

Wöhlerite has been found in several carbonatite complexes including: Prairie Lake, Ontario; Oka, Quebec; Tchivira Mt., Quilengues, Angola; Muri Mountains, Guyana; In Imanal and Anezrouf, West African Craton, Mali, and Magnet Cove, Arkansas. In this study, we include a description of the petrography of samples from the new wöhlerite-bearing localities. Electron-microprobe data are provided for wöhlerite from five of the above localities and from Brevik, Norway. A correlation of CL in wöhlerite with the electron-microprobe data indicates that the intensity of CL in wöhlerite is dependent on the Fe content.

CATHODOLUMINESCENCE INSTRUMENTATION

Cathodoluminescence is a valuable tool for the examination of carbonatites and alkaline rocks. It can be used to identify the mineral species in a complex assemblage and to reveal subtle aspects of geochemistry and petrology (Mariano 1978, 1988, Roeder et al. 1987).

A Nuclide Luminoscope was employed as the electron source, and a Gamma Scientific spectroradiometer was used to measure the CL emission spectra. The experimental conditions are the same as those described by Mariano & Ring (1975). An electron-beam diameter of approximately 2 mm was used for the generation of the CL emission spectra. Since the luminescence of wöhlerite has a moderately weak intensity, voltages of about 15 kV were usually employed, with a beam current of about 0.6 mA.

In a sample in which wöhlerite shows CL, the coloration is a moderate light greenish blue that can be readily differentiated from associated blue-luminescing apatite and feldspar (Fig. 1).

CHEMICAL ANALYSIS

The electron-microprobe analyses were performed at Queen's University using an ARL SEMQ electron microprobe. The analyses were conducted at 15 kV using energy-dispersion analysis for Si, Ti, Zr, Nb, Fe, Mn, Ca and Na, and at 25 kV for wavelength-dispersion analysis of the other elements using methods similar to those described by Roeder (1985) and Roeder et al. (1987). The energy-dispersion spectra for the wöhlerite samples do not show peaks for any other elements; thus the low analytical sum may reflect some water or excess oxygen in the structure.

The electron-microprobe data of wöhlerite from six samples are shown as columns 3 to 8 in Table 1. Analysis 3 pertains to a wöhlerite from the type locality in Brevik, Norway (Queen's University Museum collection), which was first described by Scheerer (1843). The analytical data given by Scheerer are shown in column 1 in Table 1. The tantalum oxide reported by Scheerer in 1843 was, in all probability, mainly niobium oxide (shown as such in Table 1) since most chemists, until 1844, thought that Nb and Ta were identical elements (Weast 1984).

Analysis 2, from Brögger & Cleve (1890), pertains

FIG. 1. Cathodoluminescence micrographs of wöhlerite-bearing rocks. a. Silicocarbonatite from Prairie Lake, Ontario showing light blue CL wöhlerite grains and orange calcite with associated nonluminescing pyroxene and biotite. Scale bar 0.2 mm. b. Pyroxenite from Prairie Lake, Ontario with zoned idiomorphic wöhlerite. The weak, or dark blue CL zones correlate with relatively high Fe content, as opposed to the strong, or light blue CL zones, which are low in Fe content. The zones are too narrow to determine whether or not the spectral response is different for the two zones. Scale bar 0.07 mm. c. Nepheline syenite from the Anezrouf carbonatite, Mali. The light blue-green grain in the center is a wöhlerite prism cutting into a nonluminescing nepheline grain. The equant blue grains that comprise most of the micrograph are Ti^{4+}-activated orthoclase, and the light violet grains are $LREE$-activated apatite. The orange grains are calcite, and the red bands are veins of Fe^{3+}-activated feldspar that have crystallized from late fenitizing alkaline solutions (Mariano 1988). Scale as in a and d. d. Wöhlerite in sövite from St. Lawrence Pit, Oka, Quebec. At least 3 light-blue-luminescing wöhlerite grains appear in this micrograph. Two are clearly discernible idiomorphic prisms. The dark blue grains are ovoids and clusters of $LREE$-activated apatite (Roeder et al. 1987). The matrix is Mn^{2+}-activated calcite with orange CL. The nonluminescing grains include diopside, pyrochlore and latrappite. Scale bar 0.2 mm.

TABLE 1. CHEMICAL COMPOSITION OF WOHLERITE

wt.%	1.** Brevik Scheerer (1843)	2.** Brevik Brogger & Cleve (1890)	3. Brevik	4. Guyana	5. Angola	6. Mali	7. Oka	8. Prairie Lake	9. Prairie Lake Weak CL	10. Prairie Lake Strong CL	11.** Guyana Barron & Belshaw(1978)
SiO2 =	30.62	30.12	30.30	30.35	30.22	30.09	29.88	29.92	30.40 ± 0.16	30.33 ± 0.10	30.17
TiO2 =	0.00	0.42	1.22	1.00	1.96	0.25	0.19	0.74	0.65 ± 0.24	0.51 ± 0.09	0.06
ZrO2 =	15.17	16.11	14.32	14.36	13.66	14.89	14.76	14.98	13.64 ± 0.32	14.41 ± 0.41	15.23
HfO2 =	0.00	0.00	0.58	0.29	0.19	0.24	0.11	0.17	0.17*	0.17*	0.00
Nb205 =	14.47	12.85	12.11	14.20	10.50	16.07	15.38	15.01	14.50 ± 0.61	15.24 ± 0.21	13.04
Ta205 =	0.00	0.00	0.45	0.07	0.27	0.11	0.24	0.21	0.21*	0.21*	0.06
Al203 =	0.00	0.00	0.01	0.08	0.25	0.00	0.00	0.00	0.00	0.00	0.06
Y203 =	0.00	0.00	0.61	0.08	0.20	0.07	0.11	0.06	0.06*	0.06	0.00
La203 =	0.00	0.00	0.06	0.02	0.11	0.07	0.06	0.03	0.03*	0.03*	0.00
Ce203 =	0.00	0.66	0.27	0.13	0.19	0.08	0.03	0.05	0.05*	0.05*	0.00
FeO =	2.12	1.69	1.74	0.62	1.65	0.50	0.15	0.28	0.89 ± 0.14	0.39 ± 0.14	1.20
MnO =	1.55	1.00	0.85	0.57	1.50	0.44	0.41	0.19	0.36 ± 0.06	0.34 ± 0.34	1.29
MgO =	0.42	0.12	0.27	0.15	0.27	0.12	0.37	0.12	0.12*	0.12*	0.08
CaO =	26.08	26.95	25.35	26.78	25.26	26.06	26.90	26.39	26.87 ± 0.23	26.32 ± 0.19	27.77
SrO =	0.00	0.00	0.02	0.20	0.41	0.13	0.12	0.20	0.20*	0.20*	0.00
Na2O =	8.08	7.50	7.67	7.58	7.61	7.75	7.01	7.59	7.21 ± 0.14	7.45 ± 0.17	7.77
F =	0.00	2.98	2.61	2.13	2.87	1.71	1.88	1.92	1.92*	1.92*	3.94
SUM***=	98.51	99.15	97.35	95.72	95.92	97.86	96.81	97.06	96.48	96.95	98.96

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Si =	8.359	8.046	8.219	8.184	8.248	8.159	8.158	8.147	8.294	8.247	7.995
Ti =	0.000	0.085	0.249	0.203	0.403	0.051	0.040	0.152	0.134	0.105	0.012
Zr =	2.020	2.099	1.895	1.889	1.818	1.969	1.965	1.989	1.815	1.911	1.968
Hf =	0.000	0.000	0.045	0.023	0.015	0.019	0.009	0.014	0.014	0.014	0.000
Nb =	1.786	1.552	1.485	1.732	1.296	1.970	1.899	1.848	1.789	1.874	1.563
Ta =	0.000	0.000	0.034	0.006	0.021	0.009	0.018	0.016	0.016	0.016	0.000
Al =	0.000	0.000	0.004	0.026	0.081	0.000	0.000	0.000	0.000	0.000	0.019
Y =	0.000	0.000	0.089	0.012	0.030	0.011	0.016	0.009	0.009	0.009	0.000
La =	0.000	0.000	0.007	0.002	0.012	0.007	0.007	0.004	0.004	0.004	0.000
Ce =	0.000	0.065	0.027	0.013	0.019	0.008	0.00	0.005	0.005	0.005	0.000
Fe =	0.484	0.378	0.395	0.140	0.377	0.114	0.035	0.064	0.204	0.089	0.266
Mn =	0.359	0.227	0.196	0.131	0.347	0.102	0.095	0.044	0.084	0.079	0.290
Mg =	0.171	0.048	0.110	0.061	0.110	0.049	0.151	0.049	0.049	0.049	0.032
Ca =	7.628	7.714	7.368	7.737	7.387	7.571	7.869	7.699	7.855	7.668	7.885
Sr =	0.000	0.000	0.004	0.032	0.065	0.021	0.019	0.032	0.032	0.032	0.000
Na =	4.277	3.885	4.034	3.963	4.027	4.075	3.711	4.007	3.814	3.928	3.992
F- =	0.000	2.518	2.240	1.817	2.478	1.467	1.624	1.654	1.657	1.652	3.302

*   Values the same as for analysis no. 8   *** SUM corrected for oxygen equivalent of fluorine
** Analyses from the literature

TABLE 2. STRUCTURAL FORMULAE OF WÖHLERITE

Analysis number & locality	Na4	(Ca,Fe,Mn,Mg)8	(Zr,Hf)2	(Nb,Ta,Ti)2	Si8 O34	F in (O,OH,F)2
2. Brevik-Brögger&Cleve	3.88	8.37	2.10	1.64	8.05	2.52
3. Brevik	4.03	8.07	1.94	1.77	8.22	2.24
4. Guyana	3.96	8.10	1.94	1.94	8.18	1.82
5. Angola	4.03	8.29	1.83	1.72	8.25	2.48
6. Mali	4.08	7.86	1.99	2.03	8.16	1.47
7. Oka	3.71	8.17	1.97	1.96	8.16	1.62
8. Prairie L.	4.01	7.89	2.00	2.02	8.15	1.65
9. Prairie L. Weak CL	3.81	8.20	1.83	1.94	8.29	1.65
10. Prairie L. Strong CL	3.93	7.89	1.92	1.89	8.25	1.65
11. Guyana-Barron & Belshaw	3.99	8.47	1.97	1.57	8.00	3.30

to wöhlerite from the same Brevik locality. Here, the tantalum oxide is probably combined with niobium oxide. The electron-microprobe analysis 3 has a significantly higher TiO_2 and lower ZrO_2 content than analysis 2, which may be due to an artifact of the classical wet-chemical analytical technique used by Brögger & Cleve. The classical wet-chemical technique often involved separation of a filtrate with $TiO_2 + ZrO_2 + HfO_2$ after precipitation of SiO_2. This filtrate was used to precipitate ZrO_2, but $TiO_2 + HfO_2$ could also precipitate, thus giving a high ZrO_2 and low TiO_2 content (J.R. Foster, pers. comm.). The three compositions (1–3) of Brevik

wöhlerite are remarkably similar, considering they are of different samples analyzed over a period of 145 years using quite different techniques.

The number of calculated cations for thirty-six anions for the chemical data are shown in Table 1. The cations have been summed for the structural positions in wöhlerite and are shown in Table 2 together with the theoretical structural formula. The calculated number of cations fit the theoretical structural formula quite well, although the number of cations in the silicon position is consistently above 8 (8.15–8.26) and the number of cations in the niobium position is quite variable (1.57–2.03). Mellini
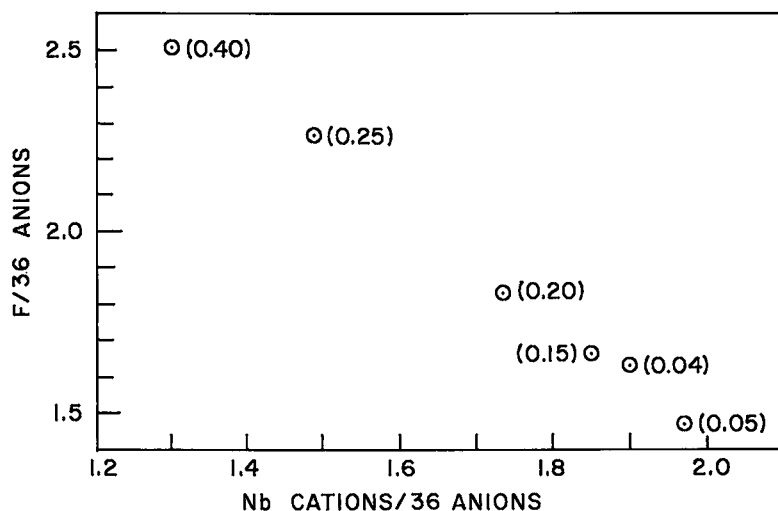
FIG. 2. Number of fluorine ions *versus* number of niobium ions on the basis of 36 anions in wöhlerite. The number of titanium cations is shown beside each point.

& Merlino (1979) suggested from their structural studies that fluorine can substitute for oxygen by a coupled substitution of Ti^{4+} for Nb^{5+}:

$$Ti^{4+} + F^{1-} \leftrightarrow Nb^{5+} + O^{2-}$$

The inverse relationship between the Nb and F content (Fig. 2) supports the coupled substitution suggested by Mellini & Merlino. The number of Ti cations is shown beside each point on Figure 2; the Ti content decreases as expected with increasing Nb content. However, the coupled substitution is more complex than the one-for-one substitution implied in the above equation since the Ti increase is only half the decrease in the Nb content. The number of cations in excess of 8 in the Ca position (Table 2) is inversely correlated with the deficiency in the Nb position, and the total of cations in these two positions is close to 10. Thus it looks as though some of the elements assigned in Table 2 to the Ca position may compensate for the deficiency in the Nb position.

INTERPRETATION OF CL EMISSION SPECTRA

As shown in the lower three spectra in Figure 3, the CL emission spectra for wöhlerite from different locations and rock types are essentially the same. They consist of a very broad emission that spans the entire visible spectrum and peaks in the blue-green at approximately 475 nm. Superimposed on this pattern is a narrower band that peaks at about 500 nm and is attributed to Mn^{2+} activation. The broad sweeping band is responsible for the whitish color of the luminescence; the more intense and narrow band gives rise to the greenish blue color.

Whereas no definitive conclusions can be made concerning the cause of CL in wöhlerite without resorting to synthesis and the controlled introduction of impurities, some speculation can be made based on chemistry and correlation with luminescence behavior in other silicates. The broad sweeping band is assumed to be intrinsic, probably associated in some way with impurities affecting the Si–O bonds; it may be enhanced by the presence of Ti. In many silicates, Ti acts to intensify an otherwise weak blue luminescence (Leverenz 1968, p. 192).

The narrow band that peaks at about 500 nm is assigned to Mn^{2+} impurity activation, based on shape and the chemical data. Iron in sufficient quantity commonly acts as a quencher of CL in minerals (Pierson 1981, Fairchild 1983). Wöhlerite from four localities shows CL, and all four contain less than 1% iron oxide; the two wöhlerite samples that do not show CL contain more than 1% iron oxide (Table 1).

The spectra for wöhlerite reported in this study, and for wöhlerite from Mont St. Hilaire, Quebec, the Red Hill syenite complex of New Hampshire, and from Magnet Cove, Arkansas, are very similar, with only small shifts in the peak emissions, which may be due to crystal-field effects. Wöhlerite, niocalite and hiortdahlite are somewhat similar in composition and structure (Nickel *et al*. 1958, Li *et al*. 1966, Merlino & Perchiazzi 1987); however, their CL emission spectra are quite different and can be used as a diagnostic tool for their identification. The CL spectrum for hiortdahlite from the Kipawa nepheline syenite
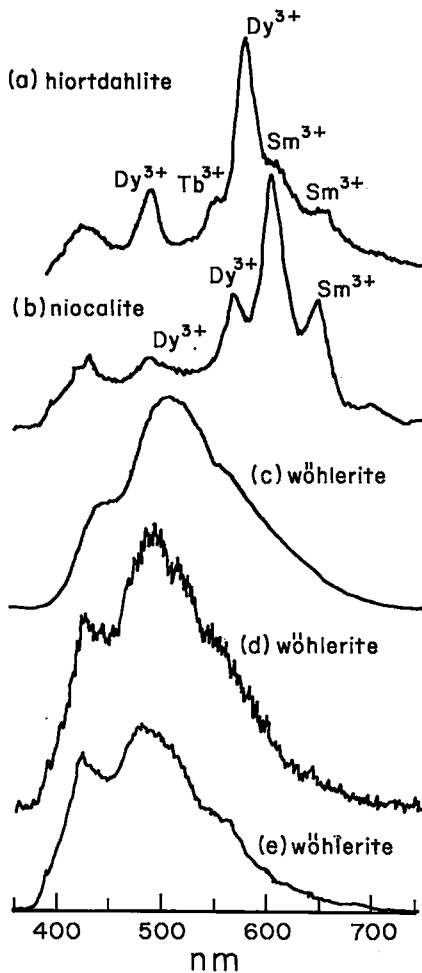
FIG. 3. Cathodoluminescence emission spectra for wöhlerite from Prairie Lake, Ontario (c), Oka, Quebec (d), and Muri Mountains, Guyana (e). The wöhlerite spectra, which are essentially identical, are compared to hiortdahlite (a) from Kipawa, Quebec and niocalite (b) from Oka, Quebec.

complex, Quebec and niocalite from Oka, Quebec (Bond Zone) are shown in Figure 3. The niocalite spectrum shows line emissions from Sm^{3+} at 600 nm, 650 nm and a small unlabeled peak at 700 nm. The presence of Sm^{3+} activation in the niocalite reflects the *LREE* dominance of carbonatite environments. In contrast, for hiortdahlite the major activator is Dy^{3+}, with line emissions at 485 and 575 nm. In addition, the strongest emission of Tb^{3+} also is resolved at 550 nm. The broad bands at 600 and 650 nm probably are due to multiple unresolved emissions from Sm^{3+} and Mn^{2+}, or they may be a result of *REE* peak overlap. The hiortdahlite spec-

trum, with peaks due to Dy^{3+} and Tb^{3+}, reflects *HREE*-dominant activation, which also is manifested in other minerals from the Kipawa Complex.

The identification of the trivalent lanthanide activators in mineral hosts is facilitated by the presence of multiple peaks for each activator, which consistently give specific wavelengths of emission regardless of the crystal-field influence of the host. Although wöhlerite crystallizes in rocks that are relatively enriched in *REE*, the *REE* have not been observed as activators in wöhlerite from any locality.

MINERALOGICAL ENVIRONMENT OF WÖHLERITE CRYSTALLIZATION

Prairie Lake, Ontario

CL in wöhlerite was first observed in rocks from the Prairie Lake carbonatite during a niobium exploration study (Mariano 1979). The Prairie Lake complex is a quasicircular plug, with an approximate surface area of 10 km². The complex has been dated at 1 Ga (Gittins *et al.* 1967, Bell & Blenkinsop 1980). The geology of the complex, based on outcrop and examination of drill core, consists of an outer annulus of sövitic rocks that grade into silicocarbonatite, ijolite and pyroxenite. The central area of the complex contains a pseudoleucite-bearing malignite that grades into ijolite and sövite. In addition to fenitization (alkali metasomatism) in parts of the complex, the malignite and ijolitic rocks contain some areas of intense Ca-metasomatism, including the formation of secondary wollastonite, pectolite and vesuvianite, whose identification is enhanced under CL examination.

Wöhlerite is a primary mineral in Prairie Lake (Fig. 4), where it occurs sporadically in the sövite, silicocarbonatite, pyroxenite, ijolite, urtite, melteigite, and malignite. The wöhlerite content reaches 7 vol.% in some of the silicocarbonatite and malignite. It usually occurs as idiomorphic to subidiomorphic prisms, and some of the crystals exhibit complex lamellar twinning.

Other niobium-bearing minerals that may occur in the same rocks with wöhlerite include pyrochlore, betafite, niobian perovskite and niobian zirconolite. The wöhlerite crystals usually are isolated from the other niobium-bearing minerals, and there is no indication of replacement. In some pyroxenite, wöhlerite contains central inclusions of niobian zirconolite and baddeleyite (Fig. 4). The wöhlerite content of the pyroxenite shown in Figures 1b and 5 is approximately 5 vol.%; it occurs in clusters and as idiomorphic prisms that exhibit color zonation when viewed in CL (Fig. 1b).

Some crystals show an inner and outer zone with decreased intensity of CL. A back-scattered electron image of the large zoned crystal at the center of Figure 1b is shown in Figure 5a. Figure 5b is an iron

X-ray image of this same crystal. The iron content seems to be higher in the central and outer zones of the crystal, which show a lower intensity of CL. Table 1 contains results of partial analyses for the less luminescent zone (analysis 9) and the more luminescent zone (analysis 10). Each composition quoted represents an average of 5 and 6 analyses, respectively, at different sites. The standard deviation from the average of each analysis is shown; the only significant compositional difference (more than two standard deviations) between sample 9 and 10 is the iron content. Iron commonly acts as a quencher for cathodoluminescence. In this sample, a difference between 0.4 and 0.9 wt.% FeO changes the intensity for the two zones, as shown in Figure 1a. The CL spectrum for the Prairie Lake wöhlerite is shown in Figure 3c. We do not know how the spectral response would change for the two zones, but assume that the color does not change, only the intensity. These crystals that show CL zoning show no zoning using normal petrographic techniques.

It is apparent from the texture that at Prairie Lake, wöhlerite is a primary mineral that crystallized during the precipitation of the more alkali components, as indicated by its concomitant formation with aegirine-augite that rims diopside cores (Fig. 4c). The zoning of the wöhlerite crystals suggests that there were at least two discrete periods of wöhlerite growth.

The Prairie Lake carbonatite is a well-mineralized niobium resource with near-surface niobium grades that approach economic values. The major niobium carrier in the complex is pyrochlore but, in some areas, wöhlerite is the dominant niobium mineral, whose recognition is best accomplished by means of CL examination.

Oka, Quebec

Although numerous studies have been conducted in various parts of the Oka carbonatite, wöhlerite had not been detected until the present study. Wöhlerite occurs as a trace mineral in søvite from the St. Lawrence Pit in Oka, where it is associated with or attached to pyrochlore and latrappite. It has not been found in the Bond Zone, where the niobium silicate *niocalite* is an accessory in soïvite from at least three trenches (Mariano 1985). The presence of niocalite and absence of wöhlerite in the Bond Zone are probably partly due to low Zr in the system, as indicated by the absence of zircon and baddeleyite. Both of these minerals, if present, would also be easily detected by CL examination

In the CL micrograph of Figure 1d, three wöhlerite crystals in søvite can be recognized by their light greenish blue luminescence, in contrast to the dark blue CL of associated apatite. Another micrograph of this søvite taken in normal polarized light also includes two wöhlerite crystals that are obscured within a cluster of apatite prisms (Fig. 6).

The fine-grained nature and scarcity of wöhlerite in the Oka søvite probably are the reasons that it has escaped recognition until now. Although the major niobium carriers at Oka are pyrochlore and perovskite, there could be an isolated area in the complex in which wöhlerite is the dominant niobium mineral, as is the case for niocalite in selected parts of the Bond Zone.

Carbonatites in Mali

During an exploration program sponsored by the United Nations Revolving Fund for Natural Resources Exploration in the eastern margin of the West African Craton, wöhlerite was discovered as an accessory mineral in nepheline syenite from two carbonatite complexes through the use of CL examination (Mariano 1983). Of four distinct but closely associated carbonatite bodies described by Sauvage & Savard (1985), the In Imanal and Anezrouf carbonatites contain accessory wöhlerite associated with pyrochlore in nepheline syenite. Both complexes include ijolite, nepheline syenite, rauhaugite, fenite and late transgressive rodbergite dikes, but wöhlerite was found only in nepheline syenite.

In the Anezrouf nepheline syenite, wöhlerite is a trace mineral occurring as disseminated blebs or hypidiomorphic crystals with an average long dimension of 50 μm. It is found attached to, or included in, nepheline, orthoclase, aegirine–augite, andradite, apatite and calcite, which suggests a lack of specific mineral association during crystallization. Late crystallizing fluorite, wollastonite and pyrite show no close association with wöhlerite crystallization. A CL micrograph of wöhlerite in nepheline syenite from the Anezrouf carbonatite is shown in Figure 1c, together with abundant violet-luminescing apatite.

In the nepheline syenite from the In Imanal carbonatite, wöhlerite was found only as an inclusion in calcite (Fig. 7), which demonstrates the close temporal relationship of crystallization between the two minerals. The common appearance of round outlines in the wöhlerite from Anezrouf and In Imanal, and their attachment or inclusion in calcite, may be a vestige texture of crystallization of immiscible carbonate and silicate liquids.

Muri Mountains, southeastern Guyana

Wöhlerite has been reported in syenite and microsyenite from the Muri Mountains, Guyana by Barron & Belshaw (1978). The average of five electron-microprobe analyses for wöhlerite from the Barron & Belshaw report is given in column 11 (Table 1), whereas the results of the microprobe analysis performed in the present study are shown in column 4. In a separate study, wöhlerite was reported in nepheline syenite from the same locality, where it was found as an accessory with pyrochlore (Mariano 1981).
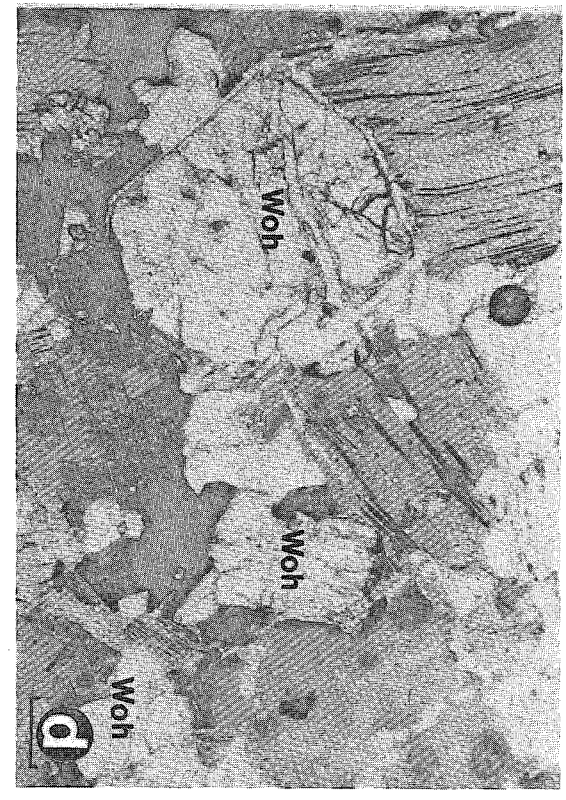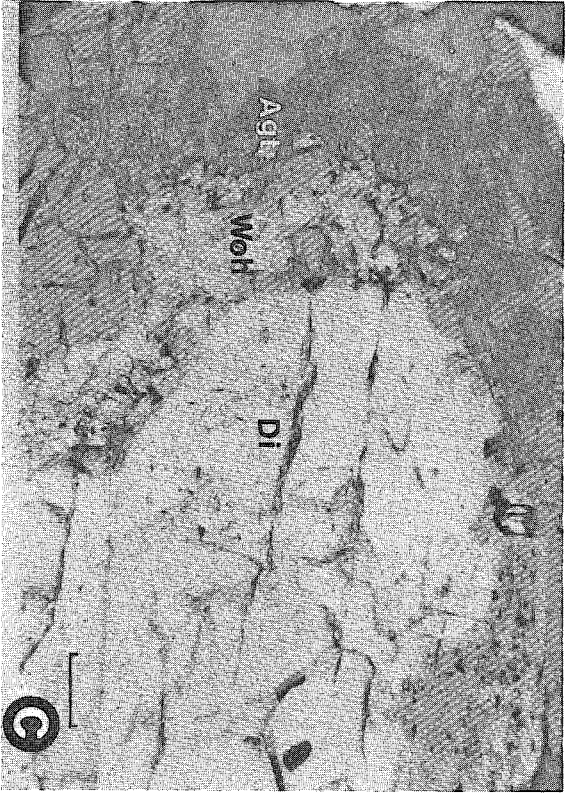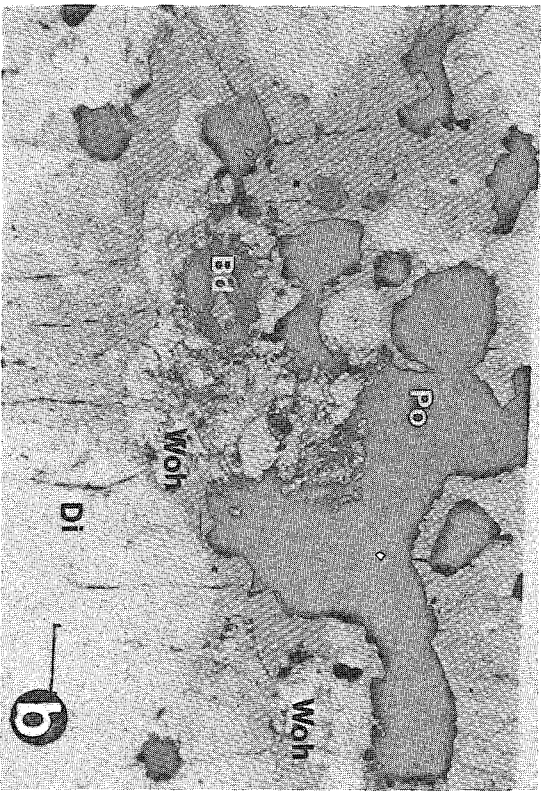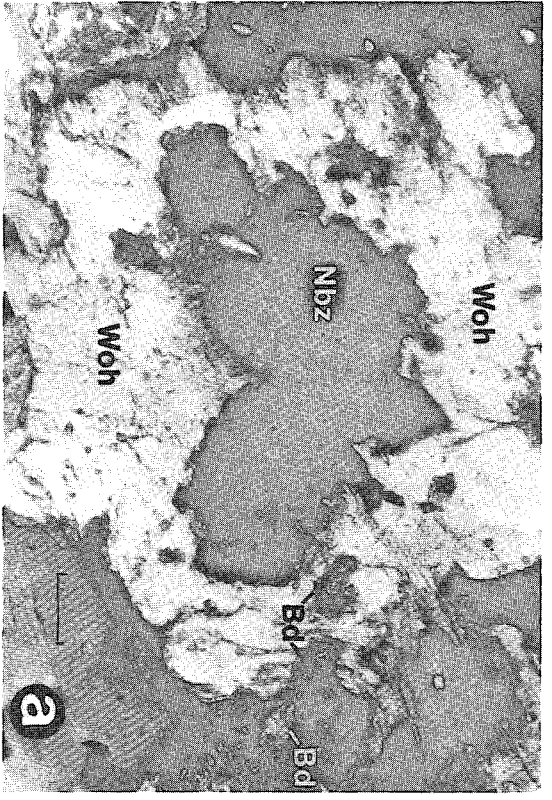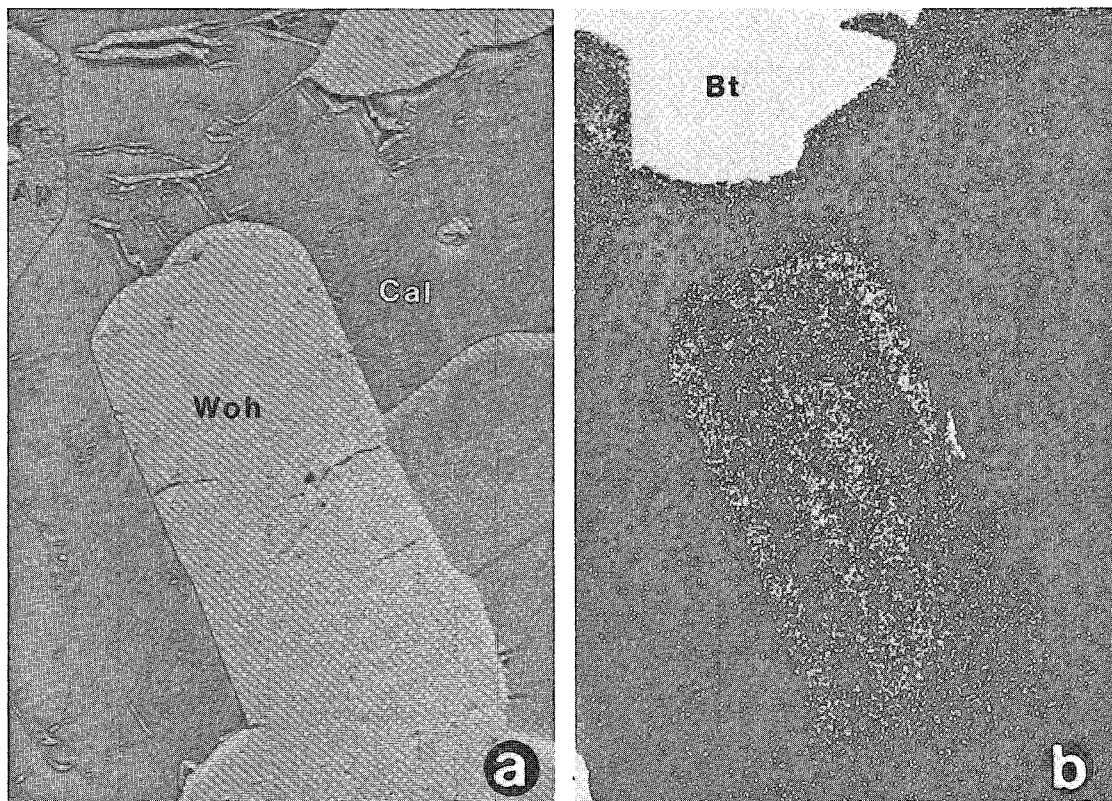
FIG. 5. A back-scattered electron image (a) and an iron X-ray image (b) of the same wöhlerite crystal from Prairie Lake as shown in the center of Fig. 1b. The X-ray image was exposed for 15 minutes to accentuate the small difference in iron content of the wöhlerite zones; as a result, the biotite (Bt) image is overexposed because of its high iron content.

Although unaltered carbonatite has not been observed either exposed in this area or from drill core taken from shallow depths, laterite mineralogy and geochemistry, and the occurrence of fenite, suggest the presence of buried carbonatite in the area (Mariano 1981). The Muri Mountain wöhlerite shows CL characteristics similar to those of the other occurrences described in this study.

Tchivira alkaline rock–carbonatite complex, Angola

In southern Angola near the town of Quilengues, two impressive mountains of Cretaceous age,

approximately 13 km apart, rise abruptly above the surrounding plains underlain by Precambrian granitic gneiss. One of the mountains, Bonga, consists predominantly of carbonatite, whereas the neighboring Tchivira is composed mostly of alkaline rocks and only subordinate carbonatite. The alkaline rocks of Tchivira include syenite, nepheline syenite, ijolite–urtite, essexite, and dike rocks including tinguaite, monchiquite and other lamprophyres.

Wöhlerite was first reported from a nepheline syenite body exposed at the highest altitude of Tchivira (2385 m) by Matos Alves (1968). He reported results of a semiquantitative X-ray-

FIG. 4. Samples from Prairie Lake, Ontario photographed in plane-polarized light and a scale bar equal to 0.14 mm, except as noted. (a) Apatite–biotite pyroxenite, with a dark central cluster of niobian zirconolite (Nbz) surrounded by polycrystalline wöhlerite (Woh) and three grains of baddeleyite (Bd) on the right. Scale bar 0.055 mm. Crossed polars. (b) Apatite–biotite pyroxenite, with a central polycrystalline cluster of wöhlerite (Woh) with baddeleyite (Bd) and opaque pyrrhotite (Po) in diopside (Di). (c) Pyroxenite with a white diopside core surrounded by polycrystalline wöhlerite that crystallized contemporaneously with aegirine-augite (Agt). (d) Silicocarbonatite that has three wöhlerite grains that appear in the color CL micrograph of Fig. 1a. Note the concentric radiation halos around the inclusions in biotite in the upper right corner.
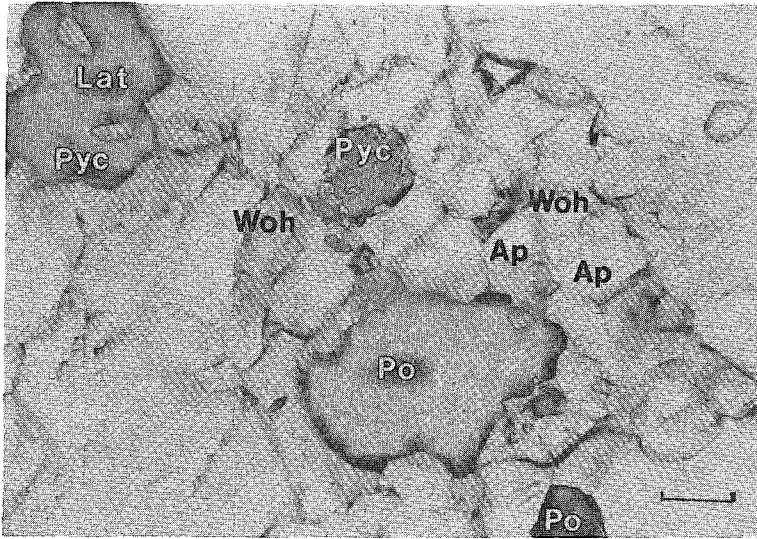
FIG. 6. Apatite sövite from St. Lawrence Pit, Oka, Quebec. The dark rectangular grain in the upper left corner of the micrograph is latrappite (Lat). The round grain with the irregular surface attached to the latrappite is pyrochlore (Pyc). Another pyrochlore grain with some translucency is isolated in the upper center. Just to the lower left of this pyrochlore is a prism of wöhlerite (Woh) that is slightly curved and points downward. The two opaque grains in the lower center are pyrrhotite (Po). Another wöhlerite grain surrounded by apatite (Ap) grains occurs on the upper right side of the largest opaque pyrrhotite grain. Photographed in plane-polarized light; the scale bar represents 0.055 mm.
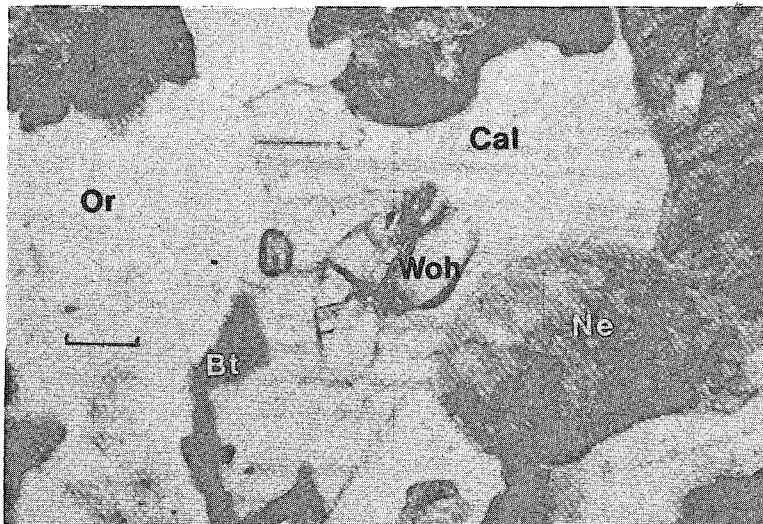

FIG. 7. Wöhlerite (Woh) grain as a central inclusion in calcite (Cal) within a nepheline syenite from the In Imanal carbonatite of Mali. The dark grains are altered nepheline (Ne), and the light grains are orthoclase (Or). The dark outline on the lower edge of the calcite is biotite (Bt). Photographed in plane-polarized light; the scale bar represents 0.14 mm.

fluorescence analysis for wöhlerite. During an exploration program for the Kennecott Copper Corp., wöhlerite from the Tchivira complex also was found in nepheline syenite from the base of the mountain (unpubl. data, Mariano 1969). The mineral occurs as idiomorphic prisms randomly disseminated throughout the rock, and in some cases intimately crystallized with niobian zirconolite. Unlike wöhlerite from the other carbonatite occurrences included in this study, the Tchivira wöhlerite contains greater than 1 wt.% FeO (analysis 5), and does not exhibit CL.

CONCLUSIONS

This study exemplifies the value of CL for the identification of obscure minerals that most often escape recognition in conventional petrographic examination. Through the use of CL, the environment of wöhlerite has been extended to carbonatite-bearing complexes, and in some cases to carbonatite and silicocarbonatite rock units within these complexes. Wöhlerite commonly is found cocrystallized with pyrochlore, latrappite, and niobian zirconolite, and in some rocks it may constitute the major source of niobium.

CL emission spectra for wöhlerite from different localities are essentially the same and consist of a broad band of luminescence that sweeps across the visible spectrum and is assumed to be intrinsic. It is modified by a narrower band that peaks at approximately 500 nm and is suspected to be from Mn^{2+} impurity activation. The CL of wöhlerite is radically different from that of niocalite and hiortdahlite, two minerals that are often compared crystallographically and chemically with wöhlerite. Niocalite and hiortdahlite both exhibit *REE* activation; the nature of the *REE* activator distribution (*LREE* or *HREE* dominance) reflects the geochemistry of their environment.

The chemical composition of six wöhlerite samples has been determined by electron-microprobe analysis. The inverse relationship between niobium and fluorine fits the structural interpretation of Mellini & Merlino (1979), who suggested a coupled substitution of $Nb^{5+} + O^{2-}$ for $Ti^{4+} + F^{1-}$. The variable intensity of CL among different wöhlerite samples is mainly a function of the ability of iron to quench CL. This is demonstrated by microprobe analyses of different zones in a crystal that shows variable CL intensity.

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