

Lithium in nigerite-group minerals

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Abstract: Nigerite-group minerals (polysomatic tin-bearing oxides) from the type locality Egbe District, Kabba Province (Nigeria) and from the abandoned tin mine of Tsomtsaub, between Omaruru and Uis in Namibia have been reinvestigated chemically and by single-crystal X-ray diffraction. At both localities nigerite occurs in quartz-sillimanite rocks associated with pegmatites. Both nigerites can be classified as 'zinconigerite-6N6S', space group $R\bar{3}m$, $a = 5.71$, $c = 55.4$ Å. In both structures the octahedral M2 site in the T_1 -layer of the nolanite module is completely occupied by Sn with minor Ti. Charge balance for the tetravalent cations is achieved by partial Li substitution for Al in adjacent octahedral sites (O-layer) sandwiched between two T_1 -layers. For the first time the presence of essential Li in nigerite-group minerals has been demonstrated by Secondary Ion Mass Spectrometry (SIMS) yielding 0.61(6) and 0.70(7) wt.% Li_2O for nigerite from Nigeria and Namibia, respectively. Associated gahnite in the Nigerian sample is free of Li_2O . Both investigated nigerite-group minerals have tetrahedral Zn : Fe > 1 in the spinel module and are therefore assigned to the zinconigerite subgroup.

It is suggested that Sn-rich nigerite-group minerals (6N6S and 2N1S polysomes) from rare-element pegmatites or skarns possess essential Li for charge balance whereas low Sn, Ti-bearing nigerites, displaying an extended solid solution with hōgbomite, do not require Li for charge balance.

Key-words: nigerite, polysomatism, crystal structure, SIMS Li analysis.

Introduction

Nigerite-group minerals comprise a polysomatic series (Neiva & Champness, 1997; Armbruster, 2002) of tin-bearing oxides occurring mainly in pegmatites, skarns, and granites. The crystal structure can be described by an ordered stacking sequence of nolanite and spinel units which can both be derived from closest oxygen packing with partial occupation of tetrahedral and octahedral voids (Grey & Gatehouse, 1979). Cubic-closest oxygen packing (ABC) is found for the spinel unit whereas a mixed packing type is characteristic of the nolanite unit (*e.g.*, two successive nolanite units have the oxygen-layer stacking sequence ACAB). The tin-bearing nolanite unit has $TM_4O_7(OH)$ stoichiometry and consists of one O-layer (for octahedral cations only) of M_3O_4 composition and one T_1 -layer (one tetrahedral cation) of $TMO_3(OH)$ composition where T and M represent tetrahedral and octahedral cations, respectively. A highly simplified composition of a nolanite module in nigerite-group minerals is $(Fe, Zn, Mg)Sn^{4+}Al_3O_7(OH)$. The spinel unit of $T_2M_4O_8$ composition consists of one O-layer and one T_2 -layer (two tetrahedral cations). Each unit is *ca.* 4.6 Å thick and their stacking periodicity determines the length of the *c*-axis of the trigonal, rhombohedral, or hexagonal members

of the polysomatic series (Hejny & Armbruster, 2002). Depending on the composition of the spinel module three subgroups are distinguished: Magnesionigerite has a spinel module of $2 \times MgAl_2O_4$ composition ($T = Mg$), ferronigerite of $2 \times FeAl_2O_4$ composition ($T = Fe^{2+}$), and zinconigerite of $2 \times ZnAl_2O_4$ composition ($T = Zn$). Members of the zinconigerite subgroup have not yet been defined as mineral species although there are several descriptions of nigerites conforming this composition (Burke *et al.*, 1977; Čech *et al.*, 1978; Neiva & Champness, 1997). The complete species name of nigerite-group minerals (Armbruster, 2002) comprises the subgroup name with a hyphenated suffix attached defining the polysome (*e.g.*, ferronigerite-6N6S).

Only two polysomes have been structurally analyzed for nigerite minerals (Grey & Gatehouse, 1979; Chen *et al.*, 1989; Arakcheeva *et al.*, 1995): 6N6S and 2N1S where the number before N and S accounts for the multiplicity of nolanite (N) and spinel (S) units in the unit cell (Armbruster, 2002). The 6N6S polysome is rhombohedral (obsolete name nigerite-24R), space group $R\bar{3}m$, with a *c*-axis in hexagonal setting of *ca.* 12×4.6 Å = 55.2 Å, whereas the 2N1S polysome is trigonal (obsolete name nigerite-6T), space group $P\bar{3}m1$, with a *c*-axis of *ca.* 3×4.6 Å = 13.8 Å. The 2N1S polysome occurs for very Sn-rich compositions because Sn

Table 1. Electron microprobe analyses for spinel and nigerites. *Li analyses by SIMS. - = not detected.

	Nigeria spinel analyses	Nigeria Esd's 5	Nigeria nigerite 23	Nigeria Esd's 23	Namibia nigerite 19	Namibia Esd's 19
SiO ₂	-	-	0.05	0.06	0.08	0.08
TiO ₂	-	-	1.51	0.41	2.24	0.74
SnO ₂	-	-	18.63	0.91	17.48	1.21
Al ₂ O ₃	56.69	0.13	54.13	0.32	54.61	0.51
Cr ₂ O ₃	0.01	0.02	0.01	0.01	-	-
Fe ₂ O ₃	0.71	0.24	-	-	-	-
FeO	15.32	0.29	9.76	0.22	9.78	0.33
MgO	1.17	0.04	0.74	0.05	0.69	0.04
MnO	0.18	0.02	0.17	0.03	0.29	0.03
ZnO	25.72	0.36	11.81	0.25	11.29	0.36
NiO	0.02	0.03	0.01	0.02	0.02	0.03
CoO	-	-	0.02	0.02	0.01	0.01
Li ₂ O*	0.004	-	0.61	0.06	0.70	0.07
Total	99.83	0.27	97.44	0.51	97.19	0.60
Spinel formula normalized to 3 cations and 8 negative charges, nigerite formula normalized to 186 negative charges						
Si	0.000		0.03		0.05	
Ti	0.000		0.80		1.18	
Sn	0.000		5.22		4.87	
Al	1.983		44.84		44.93	
Cr	0.000		0.01		0.00	
FeIII	0.016		0.00		0.00	
FeII	0.380		5.74		5.71	
Mg	0.052		0.78		0.72	
Mn	0.005		0.10		0.17	
Zn	0.564		6.13		5.82	
Ni	0.001		0.01		0.01	
Co	0.000		0.01		0.01	
Li	0.000		1.72		1.97	
Sum	3.001		65.39		65.44	

is concentrated in the nolanite module and the 2N1S polysome has a N/S ratio of 2:1 whereas the 6N6S polysome has a N/S ratio of 1:1.

If investigated by transmission electron microscopy (TEM) nigerite-group minerals exhibit superstructure reflections (Hansen & Bovin, 1982; Neiva & Champness, 1997) which can be indexed with the $a = b = 5.72 \times \sqrt{3} = 9.91 \text{ \AA}$ supercell. Furthermore, most of the individual reflections are discernable but are accompanied by continuous streaks parallel to c^* indicating stacking faults parallel to (001).

Nigerite-group minerals are closely related to högbomite polysomes where Ti⁴⁺ instead of Sn⁴⁺ is concentrated in the nolanite unit. There is also evidence for an extended solid solution series between nigerite and högbomite minerals (Schumacher *et al.*, 1987; Petersen *et al.*, 1989). Furthermore, in contrast to nigerite-group minerals högbomites exhibit a larger number of different polysomes (*e.g.*, Hejny & Armbruster, 2002). All structure refinements performed on nigerite-group minerals have in common that one octahedral position in an O-layer is only 70-75% occupied by Al with the remainder 25-30% assigned to vacancies (Grey & Gatehouse, 1979; Chen *et al.*, 1989; Arakcheeva *et al.*,

1995). Corresponding octahedral vacancies do not exist in högbomites. Thus Armbruster (1998) suggested that the described octahedral vacancies could be artifacts pretended by light octahedral cations such as Li. There are no Li analyses reported for nigerite-group minerals. Occurrence of nigerite in rare-element pegmatites actually suggests the presence of Li; in particular, Sn and Li are frequently associated in such occurrences. The suggestion of Li in nigerite (Armbruster, 1998) initiated this study, focusing on new crystal-structure refinements and Li analyses of nigerites from two different localities.

Sample description

Two samples were investigated. Sample #N17471 originates from the type locality, Egbe District, Kabba Province (Nigeria) and was obtained from the Mineralogical Museum of the University Hamburg, Germany. At the type locality nigerite occurs in a sillimanite-quartz rock associated with a cassiterite-bearing pegmatite (Jacobson & Webb, 1947; Bannister *et al.*, 1947). The second sample was collected (*ca.* 1980) by Dr. Oleg von Knorring at the abandoned tin mine of Tsomtsaub, between Omaruru and Uis in Namibia. This sample was kindly received from Paul Keller (University of Stuttgart, Germany). Von Knorring & Condlife (1985) describe this occurrence of nigerite as associated with cassiterite, columbite-tantalite, and chrysoberyl in a sillimanite-bearing quartz rock. They further remark that this assemblage is almost identical to the Nigerian type locality. Macroscopically nigerite from both localities forms golden-brown hexagonal plates, similar to mica flakes. Both studied samples are deposited at the Museum of Natural History Bern under the catalogue numbers NMBE-37035 and NMBE-37036, respectively.

Chemical analyses

Nigerite in both samples and associated gahnite in sample N17471 were analyzed with a CAMECA SX-100 electron microprobe at the GFZ Potsdam. Element concentrations were measured with wavelength-dispersive spectrometers using 15 kV accelerating potential, 20 nA beam current and a beam diameter of 1-2 μm . Peak counting times were 20 seconds for major and 30-60 seconds for minor elements; backgrounds were counted for 10-30 seconds. Standards used included the following synthetic and natural minerals and metals: wollastonite (Si, Ca); rutile (Ti); cassiterite (Sn); spinel (Mg, Al); corundum (Al); eskolaite (Cr); periclase (Mg); hematite (Fe); ilmenite (Fe, Ti); pyrophanite (Mn, Ti); gahnite (Zn, Al); NiO (Ni); metallic Co. The raw intensity data were corrected with the "PAP" program (Pouchou & Pichoir, 1985). The quality and reproducibility of the analyses was monitored by including well-characterized oxide standards in the analysis sessions. Average compositions of nigerite and gahnite with 1 σ standard deviations are given in Table 1.

Lithium in nigerite of both samples and in gahnite of sample N17471 was analyzed by Secondary Ion Mass Spectrometry (SIMS) using the Cameca ims 6f at the GFZ Pots-

dam. A primary mass-filtered $^{16}\text{O}^-$ beam was accelerated to 12.5 kV and focused to form a *ca.* 8 μm diameter beam (sample current 0.3 nA). Secondary ion yields were detected with -75 V offset, a 50 eV energy window and a mass resolution ($M/\Delta M$) of 1300. For quantifying Li in nigerite and gahnite we used the $^7\text{Li}^+ / ^{27}\text{Al}^+$ count ratio calibrated on staurolite 77-55C (0.56 wt.% Li_2O ; Holdaway *et al.* 1996; Feenstra *et al.*, 2003) and cookeite from Vanoise (2.45 wt.% Li_2O ; Vidal & Goffé, 1991). Because the Al_2O_3 contents of nigerite and gahnite compare to those of the used standards, measured $^7\text{Li}^+ / ^{27}\text{Al}^+$ count ratios required only minor corrections for absolute Al_2O_3 contents. Reproducibility of the Li_2O values obtained for nigerite from both Nigeria (7 spots analyzed) and Namibia (6 spots analyzed) was generally better than 2% relative. Considering the unknown matrix effect of Sn on the measured $^7\text{Li}^+ / ^{27}\text{Al}^+$ ratio (*cf.* Ottolini *et al.*, 2002) we increased, however, the uncertainty in Li_2O concentration to 10% relative (Table 1).

X-ray data collection

Nigerite single crystals from both localities were hand-picked from the samples and analyzed with an ENRAF NONIUS CAD4 diffractometer ($\text{MoK}\alpha$ X-radiation). Hexagonal cell parameters (rhombohedral Bravais type) for the Nigeria sample of $a = 5.716(1)$, $c = 55.444(8)$ Å and for the Namibia sample of $a = 5.7109(9)$, $c = 55.373(9)$ Å, obtained from 25 reflections with $11 < \theta < 26^\circ$, led to the identification of the 6N6S polysome. Diffraction data were collected with graphite-monochromated $\text{MoK}\alpha$ radiation up to $\theta = 40^\circ$. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf Nonius, 1983). An empirical absorption correction using the ψ -scan technique was applied. Experimental details of data collection and structure refinement are summarized in Table 2.

Several crystals tested before final data collection exhibited obverse/reverse twinning (Herbst-Irmer & Sheldrick, 2002) but such twins were disregarded because of extended data collection time (no rhombohedral extinctions). Some weak reflections in the pattern of the untwinned crystals could not be indexed and probably originate from very minor attached additional phases. Special problems occurred with the Namibia crystals because all investigated individuals displayed low crystal quality indicated by strong reflection smearing along the ω -direction. In spite of extended ω -scans uneven background was frequently encountered (particularly around weak reflections) and corresponding reflections were deleted from the data set because their integrated intensities were considered erroneous. It could well be that the uneven background is caused by satellite reflections or streaking due to (001) faults as described by TEM work (Hansen & Bovin, 1982; Neiva & Champness, 1997).

Using the space group $R\bar{3}m$ (Grey & Gatehouse, 1979; Hejny & Armbruster, 2002) the measured diffraction data were solved and refined with the programs SHELXS and SHELXL-97 (Sheldrick, 1997) applying scattering factors for neutral atoms. For disordered Fe and Zn, which cannot be distinguished by their scattering power in this type of dif-

Table 2. Data collection and refinement parameters for 'zinconigerite-6N6S'.

sample	Nigeria # N17471	Namibia
crystal size (mm)	0.20 × 0.30 × 0.05	0.25 × 0.18 × 0.05
space group	$R\bar{3}m$	$R\bar{3}m$
a (Å)	5.716(1)	5.7109(9)
c (Å)	55.444(8)	55.373(9)
θ max. ($^\circ$)	40	40
hkl (min., max.)	$10 \leq h \leq 0$ $-8 \leq k \leq 10$ $-99 \leq l \leq 0$	$10 \leq h \leq 0$ $-8 \leq k \leq 10$ $-99 \leq l \leq 0$
scan type	$1.7^\circ \omega + 0.35 \tan \theta$	$2.5^\circ \omega + 0.35 \tan \theta$
measured reflections	3490	2595 (from originally 3490 reflections those with uneven background were deleted)
observed reflections ($I > 2 \sigma(I)$)	1868	1084
unique reflections	2176	1084
number of parameters	76	76
R_{int} (%)	1.98	2.82
R_{σ} (%)	1.88	2.59
$R1$ (%)	2.01	3.49
$wR2$ (%)	5.31	8.18
Goof	1.084	1.243

fraction data, a Ni scattering curve was used, which is intermediate between Fe and Zn. In addition, low concentrations of Mg cannot be distinguished from dominant Al on the basis of scattering power. Thus Al scattering curves were used to model light elements (Mg, Al). A discussion of the Mg, Al distribution based on bond lengths and bond strengths considerations follows in a subsequent paragraph. In order to assign cations to tetrahedrally and octahedrally coordinated sites the following strategy was used: In test refinements U_{iso} of octahedrally coordinated sites was fixed at 0.004 \AA^2 and Al scattering curves were assigned to M1, M4, and M5 but a Sn scattering curve was chosen for M2. U_{iso} of tetrahedrally coordinated sites (Ni scattering curves) and of oxygen atoms was fixed at 0.005 \AA^2 and 0.007 \AA^2 , respectively. In subsequent refinements the cation population of each site was refined separately. In cases where the site population differed significantly from 1.0, a second cation species was introduced accordingly. It was found that the octahedrally coordinated sites M4, M5, and M8 are Al positions, as presumed from the beginning. This is in accordance with the structure refinement of ferrornigerite-6N6S (Grey & Gatehouse, 1979). The occupation of the octahedral position (M2) of the T_1 -layer was refined allowing for Sn and Ti leading to excellent agreement with the chemical analyses (Tab. 1). The M1 site in the O -layer of the nolanite unit displayed considerably less scattering power than expected for only Al (Grey & Gatehouse, 1979; Chen *et al.*, 1989; Arakcheeva *et al.*, 1995) and for this reason all analyzed Li was fixed at this position and for the remaining occupancy Al and vacancies were refined. The tetrahedral positions T3, T6, and T7 are occupied by (Fe, Zn) and (Mg, Al) in different ratios. After correct assignment of the cation species, an-

Table 3. Final atomic positional parameters, populations, and B_{eq} values for nigerite from Nigeria.

site	layer	population	x	y	z	B_{eq} (\AA^2)
M1	(O)	0.192 Li, 0.716(4) Al, 0.092 \square	0	1/2	0	0.64(1)
M2	(T ₁)	0.868(2) Sn, 0.132(2) Ti	2/3	1/3	0.04654	0.379(2)
T3	(T ₁)	0.335(3) (Fe, Zn) 0.665(3) Al	0	0	0.03071(1)	0.536(7)
M4	(O)	Al	0.16895(5)	0.3379(1)	0.08223(1)	0.408(6)
M5	(T ₂)	Al	0	0	0.12478(1)	0.403(8)
T6	(T ₂)	Fe, Zn	1/3	-1/3	0.13517(1)	0.527(4)
T7	(T ₂)	0.718(3) (Fe, Zn), 0.282(3) (Al, Mg)	-1/3	1/3	0.11293(1)	0.521(5)
M8	(O)	Al	-1/6	1/6	1/6	0.376(6)
O1			0.8238(2)	0.1762(2)	0.02086(2)	1.11(1)
O2			1/3	2/3	0.01737(4)	0.74(2)
H2			1/3	2/3	0.032(2)	6.32
O3			0.4944(1)	-0.4944(1)	0.06504(2)	0.59(1)
O4			0	0	0.06445(4)	0.57(2)
O5			-0.1468(1)	0.1468(1)	0.10305(2)	0.70(1)
O6			1/3	2/3	0.09994(3)	0.47(2)
O7			0.1475(1)	-0.7049(2)	0.14719(2)	0.47(1)
O8			-1/3	1/3	0.14842(4)	0.55(2)

Refined formula: $\text{Sn}_{5.21}\text{Ti}_{0.79}\text{Li}_{1.73}(\text{Fe,Zn})_{12.19}(\text{Al,Mg})_{45.32}\text{O}_{90}(\text{OH})_6$

Analyzed composition: $\text{Sn}_{5.22}\text{Ti}_{0.80}\text{Li}_{1.73}(\text{Fe}_{5.74}\text{Zn}_{6.13}\text{Mn}_{0.10})_{\Sigma=11.97}(\text{Al}_{44.84}\text{Mg}_{0.78})_{\Sigma=45.62}\text{O}_{90}(\text{OH})_6$

Table 4. Final atomic positional parameters, populations, and B_{eq} values for nigerite from Namibia.

site	layer	population	x	y	z	B_{eq} (\AA^2)
M1	(O)	0.220 Li, 0.700(9) Al, 0.08 \square	0	1/2	0	0.61(3)
M2	(T ₁)	0.803(4) Sn, 0.197(4) Ti	2/3	1/3	0.04650(1)	0.366(5)
T3	(T ₁)	0.309(5) (Fe, Zn), 0.691(5) Al	0	0	0.03071(3)	0.48(2)
M4	(O)	Al	0.1689(1)	0.3378(3)	0.08217(2)	0.44(1)
M5	(T ₂)	Al	0	0	0.12482(3)	0.42(2)
T6	(T ₂)	Fe, Zn	1/3	-1/3	0.13506(2)	0.542(8)
T7	(T ₂)	0.690(5) (Fe, Zn), 0.310(5) (Al, Mg)	-1/3	1/3	0.11293(2)	0.51(1)
M8	(O)	Al	-1/6	1/6	1/6	0.41(2)
O1			0.8232(4)	0.1768(4)	0.02089(5)	1.19(4)
O2			1/3	2/3	0.01728(9)	0.58(5)
H2			1/3	2/3	0.035(4)	6.32
O3			0.4950(3)	-0.4950(3)	0.06496(5)	0.63(3)
O4			0	0	0.06435(8)	0.61(4)
O5			-0.1477(3)	0.1477(3)	0.10302(5)	0.72(3)
O6			1/3	2/3	0.09993(8)	0.56(4)
O7			0.1475(3)	-0.7050(6)	0.14720(4)	0.51(3)
O8			-1/3	1/3	0.14836(8)	0.46(5)

Refined formula: $\text{Sn}_{4.86}\text{Ti}_{1.14}\text{Li}_{1.98}(\text{Fe,Zn})_{12.11}(\text{Al,Mg})_{45.28}\text{O}_{90}(\text{OH})_6$

Analyzed composition: $\text{Sn}_{4.87}\text{Ti}_{1.18}\text{Li}_{1.97}(\text{Fe}_{5.71}\text{Zn}_{5.82}\text{Mn}_{0.18})_{\Sigma=11.71}(\text{Al}_{44.93}\text{Mg}_{0.72})_{\Sigma=45.65}\text{O}_{90}(\text{OH})_6$

Table 5. Selected interatomic distances (\AA) for nigerite-6N6S.

		Nigeria		Namibia				Nigeria		Namibia	
M1	O2	2 \times	1.9104(11)		1.906(2)	M5	O5	3 \times	1.8881(13)		1.895(3)
	O1	4 \times	1.9784(11)		1.975(2)		O7	3 \times	1.9173(13)		1.915(3)
average			1.9557		1.952	average			1.9027		1.905
M2	O3	3 \times	1.9899(12)		1.982(3)	T6	O6	1 \times	1.953(2)		1.945(4)
	O1	3 \times	2.1087(12)		2.100(3)		O7	3 \times	1.9564(12)		1.957(3)
average			2.0493		2.041	average			1.9556		1.954
T3	O4	1 \times	1.871(2)		1.863(5)	T7	O5	3 \times	1.9260(14)		1.917(3)
	O1	3 \times	1.828(2)		1.832(4)		O8	1 \times	1.968(2)		1.962(5)
average			1.839		1.840	average			1.9365		1.928
M4	O6	1 \times	1.9006(11)		1.901(3)	M8	O7	4 \times	1.9007(7)		1.898(2)
	O3	2 \times	1.8723(9)		1.874(2)		O8	2 \times	1.9355(11)		1.935(2)
	O4	1 \times	1.9416(12)		1.940(3)	average			1.9123		1.910
	O5	2 \times	1.9524(9)		1.954(2)						
average			1.9153		1.916						

Table 6. Schematic representation of cation and oxygen stacking in nigerite-6N6S polysoms.

Stack ¹	Stack ²	Oxygen	Layer	T ^[4]	M ^[6]
C	c	O1, O2	T ₁	T3, H	M2
B	h	O3, O4	O		M4
C	c	O5, O6	T ₂	T6, T7	M5
A	c	O7, O8	O		M8
B	c	O7, O8	T ₂	T6, T7	M5
C	c	O5, O6	O		M4
A	h	O3, O4	T ₁	T3, H	M2
C	c	O1, O2	O		M1
B	c	O1, O2	T ₁	T3, H	M2
A	h	O3, O4	O		M4
B	c	O5, O6	T ₂	T6, T7	M5
C	c	O7, O8	O		M8
A	c	O7, O8	T ₂	T6, T7	M5
B	c	O5, O6	O		M4
C	h	O3, O4	T ₁	T3, H	M2
B	c	O1, O2	O		M1
A	c	O1, O2	T ₁	T3, H	M2
C	h	O3, O4	O		M4
A	c	O5, O6	T ₂	T6, T7	M5
B	c	O7, O8	O		M8
C	c	O7, O8	T ₂	T6, T7	M5
A	c	O5, O6	O		M4
B	h	O3, O4	T ₁	T3, H	M2
A	c	O1, O2	O		M1

¹conventional description of closest-packed oxygen layer-sequences

²an oxygen layer is named 'h' if adjacent layers are of the same type, a layer is named 'c' if adjacent layers display different stacking.

isotropic displacement parameters were introduced and finally a hydrogen position was extracted from difference-Fourier maps and refined without any restraints. Tables 3 and 4 list atomic coordinates, occupancies, and isotropic displacement parameters for the nigerite sample from Nigeria and Namibia. Interatomic distances are compared in Table 5.

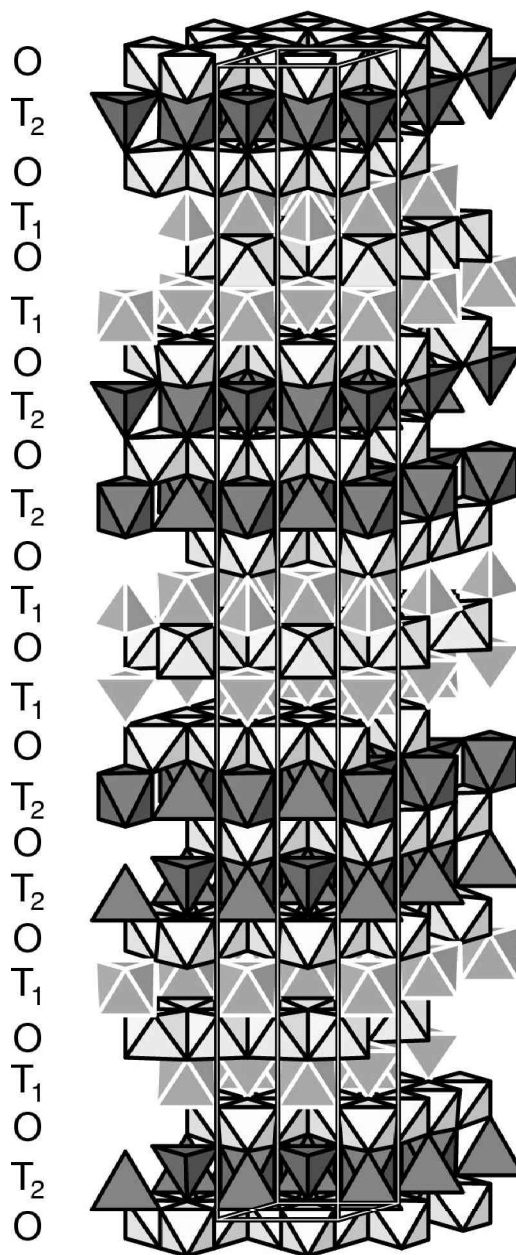


Fig. 1. Polyhedral representation of the nigerite-6N6S polysome with unit cell outlines. A layer sequence T₁, O represents a nolanite unit and a sequence T₂, O represents a spinel unit. The polysome is characterized by alternate stacking of double nolanite and double spinel units.

The 6N6S polysome is characterized by alternate stacking of double nolanite units with double spinel units (Fig. 1). Assignment of atomic sites to the various layers and units is explained in Table 6.

Nigerite crystal-chemistry

A nigerite 6N6S polysome has the composition $3 \times (T_6M_{16}O_{30}(OH)_2)$. If there are no vacancies on T or M sites and all cations are analyzed (including Li but without H), the formula can be normalized to 66 cations. If we perform

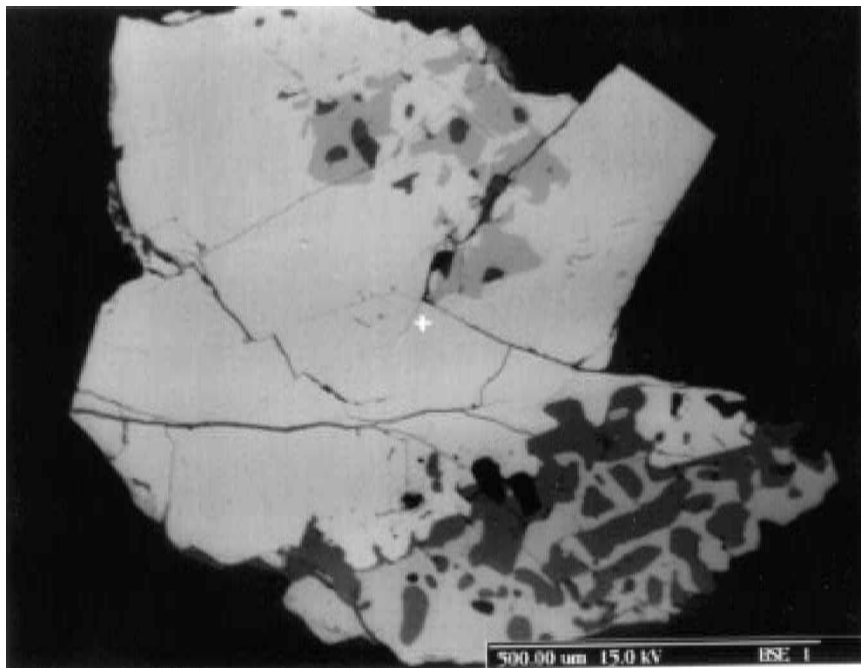


Fig. 2. Back-scattered electron image of nigerite from type locality Egbe District, Kabba Province (Nigeria). Width of picture: *ca.* 1.5 mm; light grey: nigerite; intermediate grey: gahnite; dark grey: quartz.

a corresponding calculation for both samples and assume all Fe as ferrous 187.75 and 187.64 negative charges are obtained for the Nigeria and Namibia sample, respectively. If the sample is fully hydroxylated as defined above (6 OH pfu = per formula unit) we would expect 186 negative charges. This discrepancy could indicate two things. (1) The number of cations was overestimated – there are significant vacancies in the structure –. (2) The structure is less hydroxylated as assumed from the idealized formula. There are three indicators that (1) is correct: (a) normalization to 66 cations leads to 6.08 and 6.09 (Sn+Ti) pfu for the Nigeria and Namibia sample, respectively. However, in the structure there is only one position for (Sn+Ti) incorporation yielding 6.00 (Sn+Ti) pfu. (b) Structure refinements with analyzed Li assigned as fixed element to M1 indicate in fact low concentrations of vacancies. (c) The suggestion that nigerite is not (Schumacher *et al.*, 1987; Neiva & Champness, 1997) or less hydroxylated than 6 OH pfu must be rejected for several reasons: O2 in the 6N6S polysome is only three-coordinated by $3 \times M1$. If we assume that M1 is occupied by $\frac{3}{4}$ Al and $\frac{1}{4}$ Li an average charge of 2.5^+ on M1 is obtained and each O2 receives an average bond strength of $2.5/3 = 0.833$ strongly suggesting an OH group at O2. Furthermore, the H position could be easily determined during the structure refinement. For these reasons the analyses are normalized to 186 negative charges and all Fe is assumed to be ferrous. This procedure leads to 65.39 and 65.44 cations pfu, for the Nigeria and Namibia sample, respectively. Furthermore, (Sn+Ti) reduces to 6.02 and 6.04, which is closer to the expected value of 6.00. We should keep in mind that all estimations were done for ferrous iron only but we cannot exclude low concentrations of Fe^{3+} , which would further reduce the number of cations.

According to the results of the structure refinement (Tables 3 and 4) Fe and Zn occur only in tetrahedral coordina-

tion. Electron microprobe analyses (Table 1) indicate that in both nigerites Zn is slightly dominant over Fe. Thus both minerals belong to the zinconigerite subgroup and the poly-some characterizes them as ‘zinconigerite-6N6S’. However, the composition of both crystals deviates only slightly from ferronigerite-6N6S (Zn : Fe = 1.07 (Nigeria), Zn : Fe = 1.02 (Namibia)) thus we abandoned the idea to collect physical data required for definition of a new nigerite species. Furthermore, Neiva & Champness (1997) reported chemical data of ‘zinconigerite-6N6S’ with Zn : Fe up to 7.65. These crystals are formed around a gahnite core of Zn : Fe = 16–19 indicating that Zn is strongly enriched in the spinel phase. This is also in agreement with our analyses. The Nigeria sample revealed isolated gahnite inclusions with Zn : Fe = 1.48 (Fig. 2, Table 1).

The most important result of our chemical analyses (Table 1) is that both ‘zinconigerite-6N6S’ polysomes exhibit 0.61 (Nigeria) and 0.70 wt.% Li_2O (Namibia) whereas associated spinel is essentially free of Li.

An idealized charge-balanced composition of a nolanite unit may be expressed by only three-valent cations *e.g.*, $(Al)^{T3}(Al)_4^{M1,M2,M4}O_7(OH)$ where M4 is on a general position and has to be accounted twice for formula calculation. If M2 is completely occupied by tetra-valent cations (Sn, Ti), as found for both nigerite samples, charge balance occurs on T3 by partial incorporation of (Zn, Fe) and on M1 by Li and vacancies. If all iron in our analyzed nigerites is assumed to be ferrous, charge-balanced nolanite units are obtained for both samples. This substitution mechanism is in complete agreement with the predictions and interpretations of Hejny & Armbruster (2002) based on literature data of ferronigerite-6N6S (Grey & Gatehouse, 1979), magnesianigerite-2N1S, obsolete name pengzhizhongite-6T (Chen *et al.*, 1989), and ferronigerite-2N1S (Arakcheeva *et al.*, 1995).

M2 and T3 share the T_1 -layer. Because the tin octahedron is the largest octahedron in the structure ($\langle M2-O \rangle = 2.05 \text{ \AA}$) the adjacent tetrahedral sites (T3) must be relatively small to allow adaptation of the next O -layers to the T_1 -layer. For this reason small tetrahedral cations (*e.g.*, Al) are preferred on T3 ($\langle T3-O \rangle = 1.84 \text{ \AA}$) and only a limited substitution by large divalent cations (Mg, Fe, Zn) is admissible.

In the spinel unit there is also significant Al on T7. The bulk Mg concentration of 0.78 pfu (Nigeria) and 0.72 pfu (Namibia) is too low to account for all light elements (Al + Mg) on T7 yielding 1.69 pfu and 1.86 pfu for the Nigeria and the Namibia sample, respectively. Thus there must be tetrahedral Al on T7, probably charge balanced by minor two-valent cations on octahedral positions which could not be resolved from our X-ray data. However, some Me^{2+} - Me^{3+} disorder is well documented in spinel (Andreozzi & Princivalle, 2002).

Are all nigerite-group minerals Li-bearing?

We analyzed only two samples from very similar lithologies (both from quartz-sillimanite rocks associated with pegmatites). Crystals from both samples displayed low scattering power for the M1 site which suggests, even without Li analyses, either the presence of vacancies or assumption of Li (Armbruster, 1998). This observation is common for all published nigerite structure refinements (Grey & Gatehouse, 1979; Chen *et al.*, 1989; Arakcheeva *et al.*, 1995). The sample of ferronigerite-6N6S (Grey & Gatehouse, 1979) originates from a skarn deposit, magnesionigerite-2N1S (Chen *et al.*, 1989) is from a high-temperature tungsten ore, and ferronigerite-2N1S (Arakcheeva *et al.*, 1995) is from a pegmatite. At least for these three samples we also suggest the presence of Li. If M2 in the 6N6S polysome or correspondingly M3 in the 2N1S polysome would have 30% vacancies (instead of *ca.* 20% Li) in addition to Al, the average charge on this octahedron would be only 2.1^+ yielding a bond strength of only 0.7 of the three-coordinated adjacent oxygen sites, which appears rather low even for an OH-group. Other examples for potential Li are the nigerites from rare-element granitic pegmatites of northwestern Ontario (Tindle & Breaks, 1998) where nigerite occurs associated with petalite ($LiAlSi_4O_{10}$). If the corresponding analyses are normalized to the proper number of negative charges (186 $^-$ for the 6N6S polysome and 46 $^-$ for the 2N1S polysome) significant cation vacancies are calculated suggesting Li which was not analyzed.

Potential exceptions are nigerite-group minerals displaying polysomes other than -6N6S and -2N1S. These latter polysomes have in common that the octahedral site displaying low electron density (with potential Li) is sandwiched between two Sn-rich T_1 -layers. Thus Sn^{4+} charge balance in these polysomes is obtained in directly adjacent O -layers. Nigerite-group minerals form an extended solid solution with högbomite-group minerals and it has been demonstrated (*e.g.*, Hejny & Armbruster, 2002) that in högbomites octahedral sites with low electron density ($< Al$) do not exist. Another characteristic of högbomite and extended högbomite-nigerite solid solutions is the observation that the octa-

hedral Ti, Sn site is not fully occupied by tetra-valent cations but completed by divalent cations. Thus charge balance (average cation charge of a nolanite unit is 3^+) is partially achieved on the same crystallographic site. Examples of nigerite-group minerals for which we would not expect substantial Li (because of low Sn and Ti concentrations) are the nigerites from the Falun deposit, Sweden (Schumacher *et al.*, 1987) and those from the Geco base-metal deposit, Manitouwadge, Ontario (Spry, 1982; Petersen *et al.*, 1989). For nigerites from the latter two localities the polysome has not been identified and we would tentatively expect högbomite-like polysomes as 2N2S or 2N3S, which have single nolanite-units intercalated between spinel units (Hejny & Armbruster, 2002). The 6N6S nigerite polysome has the lowest N/S ratio of the known nigerite polysomes and if normalized to 186 negative charges 6 (Sn, Ti) pfu are obtained, assuming that the M2 site is completely occupied by (Sn, Ti). If corresponding calculations are performed for nigerite from Falun (Schumacher *et al.*, 1987) only 1.9 (Sn, Ti) pfu are obtained. At Manitouwadge (Petersen *et al.*, 1989) corresponding normalization of nigerite analyses yields values between 3.7 and 5.5 (Sn, Ti) pfu.

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