Mineralogy and Petrology (1993) 48: 153–166

Mineralogy
and
Petrology

Nickenichite, a new Arsenate from the Eifel, Germany

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With 2 Figures

Received October 30, 1992;
accepted March 10, 1993

Dedicated to Prof. Dr. Josef Zemann on the occasion of his 70th birthday

Summary

Nickenichite is a new mineral found close to the village of Nickenich at the Nickenicher Sattel, Eifel, Germany. The chemical composition is $Na_xCa_yCu_z(Mg, Fe, Al)_3(AsO_4)_3$, $x \approx 0.8$, $y \approx 0.4$, $z \approx 0.4$ and was derived by means of electron microprobe analyses and by a crystal structure investigation. The latter was determined from single-crystal X-ray data: $a = 11.882(4)$ Å, $b = 12.760(4)$ Å, $c = 6.647(2)$ Å, $\beta = 112.81(2)°$, space group $C2/c$, $Z = 4$; $R = 0.053$ and $R_w = 0.033$ from 984 observed data and 102 free variables. Nickenichite is structurally related to the minerals o'danielite and johillerite. The two crystallographically different octahedrally coordinated cation positions Me = (Mg, Fe, Al) have average Me–O distances of 2.108 Å and 2.056 Å, octahedra share edges to form zig-zag chains in [10$\bar{1}$]; the chains are interconnected by AsO_4 tetrahedra. In addition the compound is characterized by partially occupied $Na^{[4+4]}$, $Ca^{[6+2]}$ and $Cu^{[4]}$ positions.

Zusammenfassung

Nickenichit, ein neues Arsenat aus der Eifel, Deutschland

Nickenichit ist ein neues Mineral, das nahe dem Ort Nickenich, am Nickenicher Sattel, Eifel, Deutschland, gefunden wurde. Die chemische Formel ist $Na_xCa_yCu_z(Mg, Fe, Al)_3(AsO_4)_3$, $x \approx 0{,}8$, $y \approx 0{,}4$, $z \approx 0{,}4$ und wurde mittels Elektronenstrahl-Mikrosondenanalysen und einer Kristallstrukturuntersuchung ermittelt. Letztere wurde mit Einkristall-Röntgendaten durchgeführt: $a = 11{,}882(4)$ Å, $b = 12{,}760(4)$ Å, $c = 6{,}647(2)$ Å, $\beta = 112{,}81(2)°$, Raumgruppe $C2/c$, $Z = 4$; $R = 0{,}053$ und $R_w = 0{,}033$ für

984 beobachtete Daten und 102 freie Variable. Nickenichit zeigt enge strukturelle Beziehungen zu den Mineralen O'Danielit und Johillerit. Die zwei kristallographisch verschiedenen oktaedrisch koordinierten Kationpositionen $Me = (Mg, Fe, Al)$ haben mittlere Me–O-Abstände von 2,108 Å und 2,056 Å, die Oktaeder werden über Kanten zu zick-zack-artigen Ketten in $[10\bar{1}]$ verknüpft, diese werden untereinander über AsO_4-Tetraeder vernetzt. Des weiteren ist die Verbindung durch partiell besetzte $Na^{[4+4]}$-, $Ca^{[6+2]}$- und $Cu^{[4]}$-Positionen charakterisiert.

Introduction

O'danielite, $Na(\underline{Zn}, Mg)_3[(AsO_4)H_2(AsO_4)_2]$, and johillerite, $Na(\underline{Mg}, Zn)_3Cu(AsO_4)_3$, are two rare minerals with closely related crystal structures which have been described by *Keller* et al. (1981a, 1982) and *Keller* and *Hess* (1988). A few synthetic arsenates(V) with similar atomic arrangements have also been investigated: $AgCo_3[(AsO_4)H_2(AsO_4)_2]$ and $AgZn_3[(AsO_4)H_2(AsO_4)_2]$ (*Keller* et al., 1981b), $AgCuCu_3(AsO_4)_3$ (*Riffel* et al., 1985), $NaCuCu_3(AsO_4)_3$ (*Pertlik*, 1987) and $KCuCu_3(AsO_4)_3$ (*Effenberger*, 1988). For comparable phosphates cf. *Antenucci* (1992) and references therein.

Recently, Mr. *N. Ballak* (Lonnig, Eifel, Germany) collected tiny crystals of an apparently new mineral. Detailed investigations showed that this mineral is closely related to the compounds mentioned above but definitely forms a separate mineral species. The idealized chemical composition is $Na_xCa_yCu_z(Mg, Fe, Al)_3(AsO_4)_3$, $x \approx 0.8$, $y \approx 0.4$, $z \approx 0.4$. The name nickenichite is derived from the type locality name: close to the village of Nickenich there is a small hill called "Nickenicher Sattel", which is one of the famous mineral deposits in the Eifel, Germany.

Mineral and mineral name were approved by the Commission on New Minerals and New Mineral Names (I.M.A.) prior to publication (#92-014). Type material is deposited at the Institut für Mineralogie und Kristallographie, Universität Wien.

Occurrence

To the north of the village of Nickenich (eastern part of the Eifel, Germany; TK 25 Bl. 5509 Burgbrohl) Devonian rocks are covered by masses of scoria (*Frechen*, 1976). These pyroclastic rocks have been produced by eruptions of two quaternary volcanos. The western volcano is called *Nickenicher Hummerich*, which still is fully covered with forest. The eastern volcano is named *Nickenicher Sattel* or short *Sattel* or sometimes *Eicher Sattel* (R 25 94 15, H 55 88 40). Unlike the *Nickenicher Hummerich* the *Nickenicher Sattel* has been intensively mined for scoria. Sometimes mining has produced clefts or even caves up to a few m in diameter. Often the faces of the cavities are covered with precipitations from fumaroles (usually hematite, rarely tenorite).

At the end of 1989 a tubular pit with a diameter of approximately 0.5 m was opened and exposed a cavity, a few m deep. The top (roof) of this inclined chimney showed a peculiar yellow to green colour. The loose yellowish-green coating of the rocks was found to be vanadinite. X-ray powder diffraction patterns of the rare green and lamellar aggregates closely assemble those of duhamelite. Further mining showed that the chimney leads to a large cave with a second chimney in which cerussite, malachite, and chrysocolla were detected by *Blass* (1992). At the top of the cave between the two chimneys Mr. *N. Ballak* detected previously unknown light blue crystals of the new mineral. Crusts of vanadinite often cover the nickenichite crystals.

Description

Nickenichite forms tiny monoclinic crystals. Individual grains are fibrous to long prismatic parallel to $[10\bar{1}]$ and often lamellar parallel to (010). The crystallographic forms $\{010\}$, $\{100\}$, and $\{10\bar{1}\}$ can be observed. Usually the crystals are radially arranged and sometimes intergrown parallel to (010). Crystals are up to 0.20 mm in length and rarely larger than 0.03 mm in diameter. Cleavage on $\{010\}$ is perfect, on $\{100\}$ and $\{10\bar{1}\}$ good, Mohs' hardness is approximately 3. The colour of nickenichite is bright blue with a pleochroism from light blue to blue. Crystals have vitreous lustre. Fluorescence effects were not observed.

Nickenichite is optically biaxial positive. The optical constants were determined on a spindle stage ($\lambda = 589$ nm): $n_x = 1.714(5)$, $n_y = 1.744(5)$, $n_z = 1.783(5)$; n_z is in the accute angle β, the angle between n_z and the *c*-axis is approximately 28° on (010), n_y is parallel to the *b* axis. The optical angle 2V was measured as 60(6)°; recalculation from the refraction indices gives 84°. The dispersion was too weak to be observed.

The chemical composition was determined by electron microprobe (EMP) analysis as well as crystal structure determination. Results of the EMP analyses are

Table 1. *Results of Electron-Microprobe Analyses for Nickenichite (operating voltage 15 kV, beam current 14 nA, diameter of electron beam 15–20 μm)*

Constituent	Weight-% (1)	Range	Standard	Theoretical (2)
P_2O_5	0.9	0.6–1.3	$AlPO_4$	0.88
V_2O_5	0.06	0.02–0.07	V_{metall}	—
As_2O_5	64.3	62.7–65.3	mimetesite	59.81
Al_2O_3	1.1	0.6–1.6	synthetic pyrope	1.09
Fe_2O_3	5.5	4.8–6.3	andradite glass	7.37
MnO	0.5	0.4–0.5	synthetic spessartine	0.38
MgO	17.9	17.1–19.0	synthetic pyrope	16.68
CuO	4.7	3.9–5.6	$SrCuSiO_4$	5.51
CaO	2.8	2.5–3.2	andradite glass	4.08
Na_2O	4.6	4.3–4.8	jadeite	4.18
K_2O	0.1	0.1–0.2	K–Ca–Mg–Al–Si glass	—
Total	102.5			100.00

Traces of SiO_2 and SO_2 have been detected, the ZnO content is below the limit of detection

Recalculation from the average chemical analysis (1):

$$Na_{0.81}K_{0.01}Ca_{0.27}Cu_{0.32}Mg_{2.42}Fe_{0.38}Mn_{0.03}Al_{0.12}As_{3.05}P_{0.07}O_{12}$$

Idealized formula from analytical data <u>and</u> structure refinement (2):

$$Na_{0.76}Ca_{0.41}Cu_{0.39}(Mg_{2.33}Fe_{0.52}Al_{0.12}Mn_{0.03})[(As_{2.93}P_{0.07})O_{12}]$$

given in Table 1. Several analysis runs yielded variable results. Obviously the cleavage of the crystals did not allow us to polish the surface perfectly. Consequently the chemical analysis alone does not give the composition of nickenichite with absolute certainty. Further analytical methods have not been employed due to lack of material. It was not possible to measure the valence state of iron experimentally. Based on charge balance considerations it is expected that at least the greater part of iron is *tri*valent. Fully occupied AsO_4 tetrahedra require nine positive charges per formula unit which points to *tri*valent iron atoms, if the positions of Na, Ca and Cu are partly occupied, the Al content is as low as found by the EMP analysis, and additional hydrogen bonds are absent. It was impossible to perform a quantitative or even semiquantitative analysis of H_2O, but crystal chemical considerations make it likely that hydrogen bonds such as found in o'danielite do not exist (see below). From a chemical point of view nickenichite is distinguished from o'danielite and johillerite, respectively, by absence of Zn, by incorporation of *tri*valent cations, and by incorporation of Ca atoms in a structural position not occupied at all in the former two minerals.

X-ray investigation

Powder diffraction data were obtained using a 57.3 mm diameter Debye-Scherrer geometry camera and Cu$K\alpha$-radiation without standard. Table 2 compares the observed and theoretical (recalculated from the refined structural data) powder patterns. The powder patterns show the close relation of nickenichite to johillerite and o'danielite (Table 3).

Preliminary single-crystal X-ray work was performed on a Weissenberg type camera. Laue symmetry $2/m$ was observed, the non-extinction rules are (hkl): $h + k = 2n$ and ($h0l$): $l = 2n$; from the possible space groups Cc and $C2/c$ the latter was confirmed by the refinement of the crystal structure. For crystal data, details of data collection, and structure refinements see Table 4.

Structure refinements were done starting from the atomic coordinates of johillerite (*Keller* and *Hess*, 1988). Some cycles of least-squares refinements indicated that the Na and Cu positions are only partially occupied. A subsequent difference Fourier summation showed an additional atomic position, which proved to be partially occupied by Ca atoms. Ca and Cu positions alternate in rows parallel [001] with a formal Ca–Cu distance of 1.662 Å; therefore a simultaneous occupation of neighbouring Ca and Cu positions within one row is impossible (there is no mutual restriction for occupations in neighbouring rows). Hence two structural models can be discussed: (A) Each of these rows exclusively is occupied either by Ca or by Cu atoms. The occupation scheme in [001] is either

model (A_1) -□-Ca-□-Ca-□-Ca-□-Ca-□-Ca-□-Ca-□-Ca-□-Ca-□-Ca- or

model (A_2) -Cu-■-Cu-■-Cu-■-Cu-■-Cu-■-Cu-■-Cu-■-Cu-■-Cu-■-

(□ and ■ are unoccupied Cu and Ca position, respectively). This gives a content of $Ca_{0.5}Cu_{0.5}$ per formula unit based on three arsenate tetrahedra, if a perfectly balanced distribution of Ca and Cu rows is assumed; but a predominance of either model (A_1) or model (A_2) enables all Ca/Cu ratios between $Ca_{0.0}Cu_{1.0}$ and $Ca_{1.0}Cu_{0.0}$. (B) Each row alternatingly contains Ca and Cu in equal amounts. This

Table 2. *Observed and Calculated Powder Pattern for Nickenichite*

h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h	k	l	d_{calc}	I_{calc}	d_{obs}	I_{obs}
1	1	0	8.3109	2	8.34	10	3	1	2	1.9724	3		
0	2	0	6.3800	25	6.37	30	4	2	−3	1.9648	2		
1	1	−1	5.8162	2			5	3	0	1.9474	4		
2	0	0	5.4764	14	5.47	10	3	5	−2	1.9397	13	1.940	10
0	2	1	4.4192	4			3	3	−3	1.9387	2		
1	1	1	4.3574	25	4.35	40	1	3	−3	1.9292	3		
2	2	0	4.1555	8	4.15	10	6	2	−1	1.8832	3		
2	2	−1	4.0343	37	4.06	50	1	1	3	1.8606	2		
3	1	−1	3.6976	22	3.69	20	1	5	2	1.8521	10	1.861	10
1	3	−1	3.5647	33	3.56	40	2	4	−3	1.8196	4		
3	1	0	3.5101	38	3.53	40	3	3	2	1.8073	6	1.809	5
2	0	−2	3.2673	6			1	7	−1	1.7558	4	1.751	5
1	1	−2	3.1957	79	3.195	60	5	3	−3	1.7405	2	1.742	5
0	4	0	3.1900	5			4	6	−1	1.7280	3		
1	3	1	3.1341	8			1	7	1	1.6964	2	1.703	5
0	0	2	3.0636	20	3.066	40	5	5	0	1.6622	3		
2	2	1	3.0478	16			6	4	−2	1.6523	9	1.654	20
2	2	−2	2.9081	6			2	0	−4	1.6505	13		
3	1	−2	2.9063	18	2.919	20	0	8	0	1.5950	2		
0	4	1	2.8295	14	2.820	10	6	4	0	1.5844	8	1.584	10
3	3	0	2.7703	7			3	7	−2	1.5557	4	1.775	5
2	4	0	2.7564	100	2.744	140	7	1	0	1.5530	2		
4	0	0	2.7382	40			2	6	−3	1.5342	2		
4	2	−1	2.6884	9	2.688	10	2	8	−1	1.5251	2	1.522	5
1	1	2	2.6340	12	2.605*	40	4	4	2	1.5239	3		
1	3	−2	2.6077	25			3	7	1	1.5123	3	1.509	5
4	0	−2	2.6038	15			1	7	2	1.5095	4		
4	2	0	2.5162	4	2.513	10	6	0	−4	1.4924	2		
5	1	−1	2.3350	3	2.325	10	8	0	−2	1.4822	4	1.483	5
2	0	2	2.3180	4			7	3	0	1.4685	2		
3	3	1	2.2846	5	2.285	10	4	4	−4	1.4541	5	1.454	5
2	4	−2	2.2825	2			7	5	−2	1.4047	2	1.405	5
4	4	−1	2.1715	2			1	7	−3	1.3943	2		
5	1	0	2.1590	6	2.159	10	0	4	4	1.3808	4	1.383	5
3	5	0	2.0917	7	2.083	10	2	0	4	1.3460	3	1.348	5
5	3	−1	2.0737	3			5	7	−3	1.3179	2	1.318	5
1	5	−2	2.0190	3	2.013	10	5	5	2	1.3085	2		
4	4	−2	2.0172	2			1	9	−2	1.3027	2	1.303	5
0	6	1	2.0091	4									
5	3	−2	1.9815	7									

* broad. Debye-Scherrer geometry, Cu$K\alpha$-radiation; reflections with $I_{calc} \geq 2$ are listed. I_{calc} is normalized to 100, I_{obs} is normalized to 140 (sum of I_{240} and I_{400} observed at the same 2ϑ angle)

causes two vacant positions between each Ca and Cu atom, with the following scheme

Table 3. *Compilation of observed powder patterns for o'danielite (Keller et al., 1981a), johillerite (Keller et al., 1982), and nickenichite (this work)*

O'danielite			Johillerite			Nickenichite		
d_{obs}	I	*hkl*	d_{obs}	I	*hkl*	d_{obs}	I	*hkl*
6.22	10	020	4.39	3	111	6.37	2	020
5.59	5	200	4.06	5	$22\bar{1}$	5.47	1	200
3.56	7	310	3.50	4	310	4.35	3	111
3.26	10	$11\bar{2}$	3.25	8	$11\bar{2}$	4.06	4	$22\bar{1}$
3.12	5	002, 131	2.75	10	330, 240	3.69	1	$31\bar{1}$
2.78*	8	$02\bar{2}$, 400, 041,	2.64	5	311, $13\bar{2}$, $40\bar{2}$	3.56	3	$13\bar{1}$
		$04\bar{1}$, 330	2.45	3	$33\bar{2}$	3.53	3	310
2.72	8	240, $42\bar{1}$	1.952	4	$13\bar{3}$, $35\bar{2}$	3.195	4	$11\bar{2}$
2.61	4	$13\bar{2}$	1.682	4	$20\bar{4}$, 460	3.066	3	002, 221
2.20	4	510, $31\bar{3}$	1.660	5	$40\bar{4}$, $71\bar{1}$, 550,	2.919	1	$31\bar{2}$
1.998	4	$53\bar{2}$, $42\bar{3}$			$64\bar{2}$	2.820	1	041
1.830	5	$24\bar{3}$, 332	1.592	3	080, $51\bar{4}$	2.744	10	240, 400
1.687	7	$64\bar{1}$, $20\bar{4}$	1.522	4	442, 153, $13\bar{4}$	2.605*	3	112, $13\bar{2}$, $40\bar{2}$
1.664	6	171, $64\bar{2}$, 460, 550	1.482	3	$80\bar{2}$, $73\bar{3}$	1.654	1	$64\bar{2}$, $20\bar{4}$
Debye-Scherrer camera,			Debye-Scherrer camera,			Debye-Scherrer camera,		
2r = 114.6 mm,			2r = 57.3 mm,			2r = 57.3 mm,		
FeKα-radiation			FeKα-radiation			CuKα-radiation		

* broad. For the strongest lines d [in Å], intensity, and Miller indices are given

Table 4. *Summary of Crystal Data, X-ray Data Collection and Structure Refinement on Nickenichite*

$a = 11.882(4)$ Å
$b = 12.760(4)$ Å
$c = 6.647(2)$ Å
$\beta = 112.81(2)^\circ$
$V = 929.0$ Å^3
space group $C2/c$
$Z = 4$
X-ray density 4.06 gcm^{-3}
$R_{int} = 0.089$
$R = 0.053$
$R_w = 0.033$
$w = [\sigma(F_0)]^{-2}$
102 variable parameters
max $\Delta/\sigma < 0.01$

54 reflections for lattice parameters
range for lattice parameters $27.5^\circ \leq 2\vartheta \leq 45.2^\circ$
crystal dimensions: $0.02 \times 0.02 \times 0.10$ mm^3
$2\vartheta/\omega$ scan mode, scan time 1.2 to 0.40°/min
scan width: 1.2° (increased for $\alpha_1 - \alpha_2$ dispersion)
3 standard reflections each 120 min
maximal variation of intensity $\pm 1.24\%$
range of data collection: $5^\circ < 2\vartheta < 70^\circ$
3242 total measured reflections ($\pm h, -k, \pm l$)
1370 unique reflections
984 reflections with $F_0 > 2\sigma(F_0)$ used for refinements
$\mu(\text{Mo}K\alpha) = 125$ cm^{-1}
absorption correction according to crystal shape
transmission factors from 0.589 to 0.714

STOE four circle diffractometer AED2, Mo tube, graphite monochromator; computer program STRUCSY on an ECLIPSE S140 computer (Data General).
Data were corrected for Lorentz and polarization effects, neutral complex scattering functions from the International Tables for X-ray Crystallography (1974) were used. The secondary isotropic extinction (*Zachariasen*, 1967) is $g = 2.0(8) \cdot 10^{-6}$.

Table 5. *Structural Parameters (E.s.d.'s in Parentheses) for Nickenichite*

Atom	Occupation	Wyckoff letter	Site symmetry	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Na	0.76(1)	4(*e*)	2	0.0	0.9922(5)	0.25	0.018(3)	0.034(4)	0.030(3)	0.0	0.001(2)	0.0	2.34
Ca	0.41(1)	4(*b*)	$\bar{1}$	0.0	0.5	0.0	0.041(4)	0.010(3)	0.033(3)	−0.003(2)	−0.010(3)	0.001(2)	2.77
Cu	0.39(1)	4(*e*)	2	0.0	0.5026(2)	0.25	0.014(2)	0.005(2)	0.030(2)	0.0	0.007(2)	0.0	1.33
Me(1)	1.0*	4(*e*)	2	0.0	0.2616(3)	0.25	0.028(2)	0.016(2)	0.022(2)	0.0	0.009(2)	0.0	1.74
Me(2)	1.0*	8(*f*)	1	0.2143(1)	0.1558(1)	0.1244(3)	0.0162(9)	0.0091(9)	0.0147(9)	0.0005(7)	0.0078(8)	0.0013(8)	1.01
As(1)	1.0	4(*e*)	2	0.0	0.71180(8)	0.25	0.0166(5)	0.0073(5)	0.0128(5)	0.0	0.0045(4)	0.0	0.99
As(2)	1.0	8(*f*)	1	0.26733(6)	0.38706(6)	0.3757(1)	0.0164(3)	0.0081(3)	0.0139(4)	−0.0003(3)	0.0063(3)	−0.0003(4)	1.00
O(11)	1.0	8(*f*)	1	−0.1085(4)	0.6232(4)	0.2381(9)	0.019(2)	0.013(2)	0.027(3)	−0.005(2)	0.008(2)	0.003(3)	1.56
O(12)	1.0	8(*f*)	1	−0.0386(4)	0.7840(4)	0.0200(8)	0.011(2)	0.024(3)	0.011(2)	−0.003(2)	0.004(2)	0.006(2)	1.21
O(21)	1.0	8(*f*)	1	0.1169(4)	0.3933(4)	0.3150(8)	0.015(2)	0.012(2)	0.025(3)	0.000(2)	0.011(2)	−0.005(2)	1.28
O(22)	1.0	8(*f*)	1	0.2838(4)	0.3141(4)	0.1785(7)	0.019(2)	0.010(2)	0.012(2)	−0.001(2)	0.007(2)	−0.004(2)	1.05
O(23)	1.0	8(*f*)	1	0.3325(4)	0.5042(4)	0.3887(8)	0.018(3)	0.014(3)	0.022(3)	−0.004(2)	0.009(2)	0.000(2)	1.42
O(24)	1.0	8(*f*)	1	0.3397(4)	0.3294(4)	0.6189(8)	0.020(2)	0.012(2)	0.011(2)	0.001(2)	0.005(2)	0.003(2)	1.15

* Least-squares refinements with *Me* = (Mg, Fe) gave *Me*(1) = $Mg_{0.89}Fe_{0.11}$ and Mg(2) = $Mg_{0.78}Fe_{0.22}$

The anisotropic displacement parameter is defined as $\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{i=1}^{3} U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, B_{eq} after *Fischer* and *Tillmanns* (1988)

Table 6. *Interatomic Distances* (Å) *and Bond Angles* (°) *for Nickenichite*

Me(1)	O(12)	O(12)	O(24)	O(24)	O(21)	O(21)
O(12)	2.100(5)	4.035(10)	2.559(7)[a]	2.910(7)	3.055(7)	3.512(7)
O(12)	147.9(3)	2.100(5)	2.910(7)	2.559(7)[a]	3.512(7)	3.055(7)
O(24)	74.9(2)	87.5(2)	2.109(5)	3.522(9)	2.891(7)	4.158(7)
O(24)	87.5(2)	74.9(2)	113.2(3)	2.109(5)	4.158(7)	2.891(7)
O(21)	92.9(2)	112.9(2)	86.4(2)	159.7(3)	2.115(5)	2.569(9)
O(21)	112.9(2)	92.9(2)	159.7(3)	86.4(2)	74.8(3)	2.115(5)

Me(2)	O(11)	O(23)	O(24)	O(22)	O(12)	O(22)
O(11)	1.986(5)	2.890(7)	3.292(7)	2.859(7)	4.043(7)	2.709(7)
O(23)	92.8(2)	2.004(5)	2.801(7)	3.207(7)	3.062(7)	4.155(7)
O(24)	109.3(2)	87.4(2)	2.051(5)	4.029(7)	2.559(7)[a]	2.974(7)
O(22)	89.9(2)	104.2(2)	157.2(5)	2.059(5)	2.727(7)	2.734(10)[b]
O(12)	168.6(3)	97.2(2)	76.6(2)	82.5(2)	2.077(5)	2.968(7)
O(22)	81.5(2)	172.5(3)	89.9(2)	80.8(3)	88.9(2)	2.159(5)

Na–O(23) = 2.455(5), 2x
Na–O(23) = 2.502(4), 2x
Na–O(24) = 2.878(7), 2x
Na–O(12) = 3.011(8), 2x
Na–O(22) = 3.323(6), 2x

Ca–O(11) = 2.329(5), 2x
Ca–O(21) = 2.432(4), 2x
Ca–O(21) = 2.573(4), 2x
Ca–O(11) = 2.867(4), 2x

Cu–O(21) = 1.896(5), 2x
Cu–O(11) = 1.989(5), 2x

As(1)	O(12)	O(12)	O(11)	O(11)	As(2)	O(23)	O(21)	O(24)	O(22)
O(12)	1.689(5)	2.831(10)	2.817(7)	2.770(7)	O(23)	1.671(4)	2.799(7)	2.688(7)	2.747(7)
O(12)	113.9(4)	1.689(5)	2.770(7)	2.817(7)	O(21)	113.6(3)	1.675(4)	2.758(7)	2.678(6)
O(11)	112.8(3)	110.0(3)	1.694(5)	2.522(9)[c]	O(24)	106.8(3)	110.7(3)	1.678(5)	2.746(7)
O(11)	110.0(3)	112.8(3)	96.2(3)	1.694(5)	O(22)	110.2(3)	105.9(2)	109.7(3)	1.680(4)

[a] common O–O edge between a *Me*(1)O_6 and a *Me*(2)O_6 octahedron
[b] common O–O edge between two *Me*(2)O_6 octahedra
[c] common O–O edge between an AsO_4 tetrahedron and a CuO_4 square or a CaO_8 cube, respectively

model (*B*) -Cu-■-□-Ca-□-■-Cu-■-□-Ca-□-■-Cu-■-□-Ca-□-■-Cu-

and the formula content is $Ca_{1/3}Cu_{1/3}$. Because nickenichite contains $Ca_{0.4}Cu_{0.4}$, it is expected that the arrangement of Ca and Cu atoms is statistical but intermediate between model (*A*) and model (*B*), also changes between the different models within one row seem to be possible. In addition, on strongly exposed single crystal X-ray photographs no interlayer reflections or even weak streaks were detected which would be expected if either only model (*A*) or only model (*B*) is verified.

The two octahedrally coordinated *Me* positions are expected to have occupation factors $n_{Me} = 1.0$, $Me =$ Mg, Fe, Al, and Mn (Mg is the main constituent; only small amounts of Fe and Al as well as traces of Mn occur). Due to the similar atomic numbers of Mg and Al or Fe and Mn only scattering functions for Mg and Fe were used for all calculations; the ratio of the occupation factors n_{Mg}/n_{Fe} was allowed to vary during refinements but $n_{Me} = n_{Mg} + n_{Fe}$ was fixed to 1.0 during structure refinements. Final structural parameters are given in Table 5, selected interatomic distances and bond angles are compiled in Table 6.

Discussion

Dominant crystal chemical features of the crystal structure of nickenichite are very similar to those of the structurally related compounds (see Table 7). The common

Table 7. *Comparison on minerals and synthetic compounds structurally related to nickenichite: cell parameters* (space group C2/c) *and average cation-anion bond lengths* (in Å) *for analogue atomic positions are given*

	o'danielite $Na(\underline{Zn}, Mg)_3[(AsO_4)H_2(AsO_4)_2]$		johillerite $NaCu(\underline{Mg}, Zn)_3(AsO_4)_3$		nickenichite $Na_{0.8}Ca_{0.4}Cu_{0.4}(\underline{Mg}, Fe, Al)_3(AsO_4)_3$		$AgCo_3[(AsO_4)H_2(AsO_4)_2]$		$AgZn_3[(AsO_4)H_2(AsO_4)_2]$		$AgCuCu_3(AsO_4)_3$		$NaCuCu_3(AsO_4)_3$		$KCuCu_3(AsO_4)_3$	
a [Å]	12.113(3)		11.870(3)		11.882(4)		12.159(9)		12.169(2)		12.127(2)		12.051(1)		12.234(5)	
b [Å]	12.445(4)		12.755(3)		12.760(4)		12.438(7)		12.495(3)		12.490(2)		12.420(1)		12.438(5)	
c [Å]	6.793(1)		6.770(2)		6.647(2)		6.782(3)		6.755(1)		7.278(1)		7.290(1)		7.307(3)	
β [°]	112.87(1)		113.42(2)		112.81(2)		113.16(3)		112.77(1)		117.94(1)		118.10(1)		118.17(2)	
V [Å^3]	943.5		940.5		929.0		943.0		947.1		973.9		962.5		980.2	
t_{101} [Å]	11.354		11.084		11.141		11.357		11.405		10.832		10.752		10.893	
$t_{10\bar{1}}$ [Å]	16.026		15.831		15.704		16.084		16.042		16.815		16.767		16.955	
d_{101} [Å]	4.731		4.658		4.636		4.714		4.725		4.637		4.622		4.648	
$M^{1+,[4+4]}$	Na	2.697	Na	2.684	$Na_{0.76}$	2.712	Ag	2.731	Ag	2.743	Ag	2.677	Na	2.633	K	2.712
$M^{2+,[6+2]}$	vacant		vacant		$Ca_{0.41}$	2.550	vacant		vacant		vacant		vacant		vacant	
$M^{2+,[4\,\mathrm{square}]}$	vacant		Cu	1.930	$Cu_{0.39}$	1.943	vacant		vacant		Cu	1.926	Cu	1.911	Cu	1.917
hydrogen bond	H	2.502	*	2.918	*	2.952	H	2.505	H	2.539	*	2.955	*	2.936	*	2.963
$Me(1)^{2+,3+,[6]}$	$(\underline{Zn}, Mg)$	2.154	(Mg, Zn)	2.121	(Mg, Fe, Al)	2.108	Co	2.135	Zn	2.147	Cu	2.158	Cu	2.156	Cu	2.162
$Me(2)^{2+,3+,[6]}$	$(\underline{Zn}, Mg)$	2.104	$(\underline{Mg}, Zn)$	2.082	$(\underline{Mg}, Fe, Al)$	2.056	Co	2.098	Zn	2.103	Cu	2.113	Cu	2.108	Cu	2.120
As(1)$^{[4\ \mathrm{tetrahedron}]}$	As	1.694	As	1.688	As	1.692	As	1.697	As	1.703	As	1.710	As	1.704	As	1.701
As(2)$^{[4\ \mathrm{tetrahedron}]}$	As	1.695	As	1.688	As	1.676	As	1.694	As	1.688	As	1.690	As	1.691	As	1.687
reference	1		1		this work		2		2		3		4		5	

* Compound containing no hydrogen bond; instead the analogue O–O distance is given (an edge in the CuO_4 square or CaO_8 cube, respectively)
References: 1: *Keller* and *Hess* (1988); 2: *Keller* et al. (1981b); 3: *Riffel* et al. (1985); 4: *Pertlik* (1987); 5: *Effenberger* (1988)

structural units are zig-zag chains in [10$\bar{1}$] formed by the edge connection of more or less distorted $Me^{2+,3+}O_6$ octahedra. AsO_4 tetrahedra interconnect these $^{1}_{\infty}[MeO_4]_3$ chains to a three dimensional network. While for *Me* atoms the elements Mg, Al, Mn, Fe, Co, Cu, and Zn are known, the tetrahedra are practically exclusively occupied by As atoms. The $^{3}_{\infty}[Me_3^{2+,3+}(AsO_4)_3]$ net has two types of channels parallel [001]: channel *I* houses *mono*valent atoms like Na, K or Ag in a [4 + 4] or even [8] coordination. Channel *II* has three different atomic positions each of which is occupied in at least one compound: the [6 + 2] coordinated Ca atom, the square planar [4] coordinated Cu atom, and hydrogen atoms forming short hydrogen bonds. The crystal structure of nickenichite is characterized by distinct coordination polyhedra: the MeO_6 octahedra have to be considered as occupied by different cations caused by the complex chemical composition and the positions for Na, Ca and Cu are partially vacant. Figure 1 depicts the principal connection type of the crystal structure.

The MeO_6 octahedra: In nickenichite the two crystallographically different *Me* sites have moderately distorted octahedral environments of O atoms. Due to edge sharing of MeO_6 octahedra the common O–O edges are shortened and the corresponding O–*Me*–O angles are smaller than the others. The *Me*(1) atom shows a stronger angular distortion whereas the *Me*(2) atom has a larger variation of the individual *Me*–O bond lengths. The average bond length ⟨*Me*(1)–O⟩ exceeds ⟨*Me*(2)-O⟩ by 0.046 Å. Least-squares refinements gave a slight enrichment of Mg (and Al) on *Me*(1) as compared to the *Me*(2) position for which calculations gave a higher Fe (and Mn) content. Correlating ⟨*Me*–O⟩ bond distances and ionic radii one would expect that the cation with the largest ionic radius (Mg, $r = 0.72$ Å) predominantly occupies the *Me*(1) position whereas the smallest cation under consideration (Al, $r = 0.535$ Å) occupies *Me*(2) due to the size of the coordination polyhedra; the intermediate cations (Fe, $r = 0.645$ Å) should then predominantly occupy the *Me*(2) position because the *Me*(1) position can be filled solely with Mg atoms (ionic radii from *Shannon*, 1976). From these facts a clear allocation of the chemical constituents to the two *Me* positions still is open for discussion.

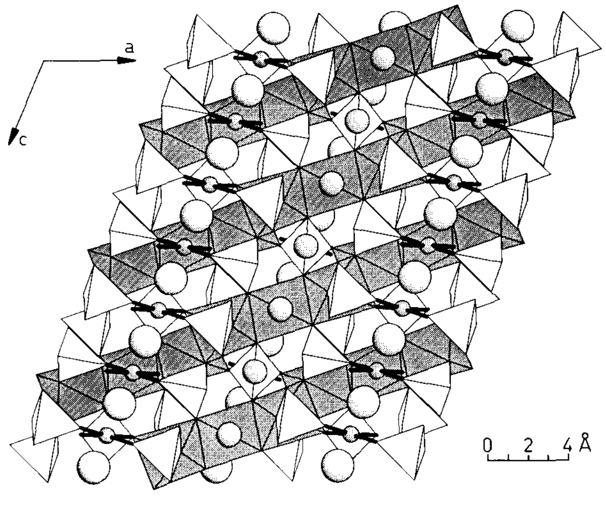

Fig. 1. Part of the crystal structure of nickenichite with the cations in $0.0 \leq y \leq 0.5$ projected on (010). The $^{1}_{\infty}[MeO_4]_3$ chain parallel to [$\bar{1}$01] and the AsO_4 tetrahedra are dark and light shaded, respectively. The atoms Cu, Na and Ca are labelled as small, medium and large spheres; in addition the Cu–O bonds are indicated by broad sticks (program ATOMS: *Dowty*, 1991)

It is worthy to note that all crystal structures related to that of nickenichite have $\langle Me(1)\text{–O}\rangle$ larger than $\langle Me(2)\text{–O}\rangle$. $Me(1)O_6$ and $Me(2)O_6$ are nearly regular octahedra for Me = Mg, Co and Zn; on the other hand a strong distortion towards a tetragonal dipyramidal [4 + 2] environment is observed for Cu^{2+} atoms as expected from the Jahn-Teller effect (*Zemann*, 1961, 1972).

The AsO_4 tetrahedra: The As^{5+} atom is tetrahedrally coordinated by O atoms. As found for the other structurally related compounds the average bond distance $\langle$As(1)–O$\rangle$ is larger than $\langle$As(2)–O$\rangle$; the shortest $\langle$As–O$\rangle$ is observed in nickenichite for the As(2) atom. The $As(1)O_4$ tetrahedron and the CuO_4 square or CaO_8 cube, respectively, share a common O(11)–O(11) edge, which is shortened to 2.522(9) Å, As(1)–Cu is 2.669(3) Å, As(1)–Ca is 3.173(1) Å. Consequently it seems probable that the minor P content detected by microprobe-analyses in nickenichite replaces As(2).

The sharing of an O–O edge between a CuO_4 square and an AsO_4 group within the type structures under discussion obviously causes that compounds containing phosphate instead of arsenate tetrahedra in principal form a different structure type: *e.g.*, the crystal structure of the compound $KCu_4(PO_4)_3$ (*Effenberger*, 1987) is quite different with two of the four Cu atoms in a strikingly regular trigonal dipyramidal CuO_5 coordination. PO_4 tetrahedra and $Cu^{[4+1]}O_5$ polyhedra (tetragonal pyramids) sharing common edges are known, but this edge is between O atoms forming a "short" and the additional fifth Cu–O bond length (see α-$NaCuPO_4$, *Quarton* and *Kolsi*, 1983, or orthorhombic $KCuPO_4$, *Effenberger*, 1984).

Channel I containing Na atoms: The Na atom has a distinct [4 + 4] coordination which can be best described as formed by two penetrating coordination figures: the average $\langle$Na–O$\rangle$ bond distance for the four nearest neighbours is 2.479 Å; the O atoms are arranged in an approximate square in (010): O–Na–O is 84.3(2)° and 95.6(2)°, and 173.0(3)° and 177.9(3)°, respectively. The O atoms of the four longer bonds form a disphenoid elongated parallel [010]: O–Na–O angles are 56.1(5)°, 75.44°, 126.3(2)° and 143.6(2)°. O–Na–O angles between near and distant O atoms are from 59.9(2)° to 118.2(2)°. As shown in Fig. 2a, the NaO_4 squares are edge connected to form rows in [001]. In the crystal structures related to that of nickenichite the position of Me^{1+} has varying coordination numbers from [4 + 4] to [8] depending on the type of *Me* and on the requirements of the other positions. The most regular [8] coordinations were found for the compounds $Me^{1+}CuCu_3(AsO_4)_3$ with Me^{1+} = Na, K, and Ag, the most pronounced [4 + 4] coordinations were found for compounds with an $[(AsO_4)H_2(AsO_4)_2]$ group.

Channel II containing Ca and Cu atoms (and hydrogen atoms): The occupation of the Ca position is known only from nickenichite. It is a [6 + 2] coordinated position with $\langle$Ca–O$\rangle$ = 2.445 Å for the near and twice 2.847(4) Å for the distant oxygen atoms. The coordination figure is a distorted cube, for *cis*–O atoms the angles O–Ca–O vary from 57.0(3)° to 123.1(3)°; for *trans*-arranged O atoms O–Ca–O is 180° by symmetry. With r.m.s. amplitudes of 0.277, 0.138 and 0.099 Å, the displacement parameters of the Ca atom has the largest anisotropy of any atom.

The Cu atom is coordinated by O atoms in form of a distorted square with an average $\langle$Cu–O$\rangle$ bond distance of 1.943 Å. Further Cu–O bond distances are larger

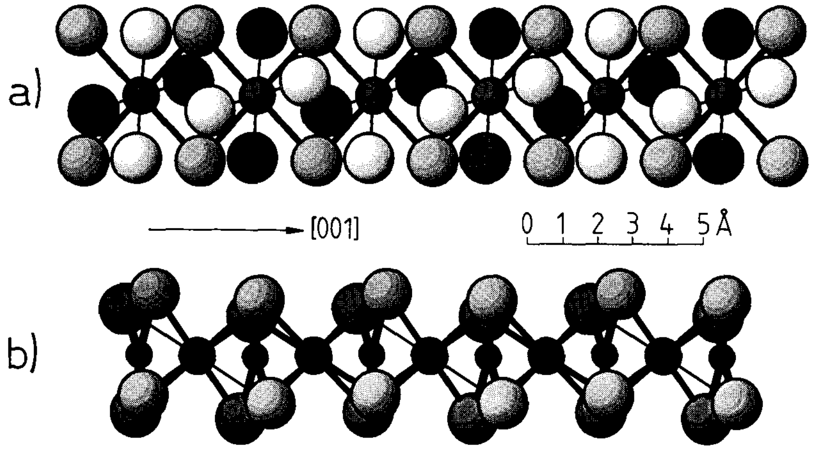

Fig. 2. The two channels in the crystal structure of nickenichite running parallel to [001] (vacancies, even if caused by crystal chemical requirements in channel *I* are not taken into consideration). (a) Channel *II* is solely occupied by sodium atoms: short Na–O bonds are shown by bold lines, the four additional Na–O bonds are indicated by thin lines. The edge sharing NaO_4 squares are in the projection plane (010). Na and O atoms are small and large spheres. (b) Channel *II* is formed by face sharing CaO_8 cubes with the CuO_4 squares within the common faces. Atoms O, Ca and Cu are large, medium and small spheres, long and short Ca–O bonds are indicated by bold and thin lines, Cu–O bonds are medium in thickness (program ATOMS: *Dowty*, 1991)

than 3.50 Å. O–Cu–O bond angles deviate definitely from rectangularity due to edge connection of the CuO_4 square to two AsO_4 tetrahedra; this causes an elongation of the square towards a rectangle with angles O(11)–Cu–O(11) = 78.7(3)° and O(21)–Cu–O(21) = 85.3(3)°, the others are 98.9(2)° and 169.8(4)°.

Full occupation of Ca atom positions would require the connection of the CaO_8 cubes via each two opposite faces to rows in [001]. As shown in Fig. 2b, the CuO_4 square represents the common face (for models concerning the possible occupation schemes see section "X-ray investigation" of this paper).

In o'danielite as well as in the two inorganic compounds $AgCo_3[(AsO_4)H_2(AsO_4)_2]$ and $AgZn_3[(AsO_4)H_2(AsO_4)_2]$ short hydrogen bonds $O(11)\cdots H\cdots O(21)$ from 2.502 Å to 2.539 Å occur in two opposite edges of the "$\square O_4$ square" (corresponding to the CuO_4 square in johillerite, □ is a vacant position). It should be mentioned that the equivalent distance $O(11)\cdots O(21)$ in nickenichite is 2.952 Å and agrees well with the distances found in related compounds without hydrogen (2.918 Å to 2.963 Å). Neither O(11) nor O(21) have larger anisotropic displacement parameters. Therefore a significant hydrogen content in nickenichite incorporated in the crystal structure similar to o'danielite can be excluded from the discussion. On the other hand the absence of hydrogen atoms in nickenichite supports the presence of Fe^{3+} because of charge balance requirements.

Comments on variations of unit cell and chemical composition: The unit cell dimensions of the crystal structures related to nickenichite are predominantly controlled by the different space requirements of the MeO_6 polyhedra and by the formation of the $[(AsO_4)H_2(AsO_4)_2]$ group. The largest values for $t_{10\bar{1}}$ (direction of the

$^{1}_{\infty}[\mathit{Me}\mathrm{O}_4]_3$ chains) occur, if the *Me* atom positions are occupied by the [4 + 2] coordinated Cu atoms instead of [6] coordinated atoms; simultaneously t_{101} is decreased. The two long Cu–O bonds in the tetragonal dipyramidal $\mathrm{Cu}^{[4+2]}\mathrm{O}_6$ polyhedron are approximately parallel [001] for both crystallographically different $\mathit{Me}\mathrm{O}_6$ polyhedra; as a result the lattice parameter *c* is definitely longer for *Me* = Cu than for the other compounds. The incorporation of the $[(\mathrm{AsO}_4)\mathrm{H}_2(\mathrm{AsO}_4)_2]$ group increases d_{101} (separation of the $^{1}_{\infty}[\mathit{Me}\mathrm{O}_4]_3$ chains) from ≈4.64 Å to ≈4.72 Å; t_{101} and $t_{10\bar{1}}$ are enlarged as compared to compounds without hydrogen bonds but $\mathit{Me}\mathrm{O}_6$ octahedra.

Acknowledgements

Mr. *N. Ballak*, Lonnig, Eifel, Germany, kindly made crystals of nickenichite available for our investigations. Thanks are due to Mag. Dr. *G. Giester*, Doz. Dr. *Ch. Köberl*, Dr. *Ch. Lengauer*, and Mag. Dr. *M. Wildner* for various help and fruitful discussions. Financial support by JCPDS/ICDD, Swarthmore, PA, USA, is gratefully acknowledged. The constructive criticism of two Mineralogy and Petrology reviewers is appreciated.

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