

²⁹Si AND ²³Na MAS NMR SPECTROSCOPIC STUDY OF THE POLYTYPES OF THE TITANOSILICATE PENKVIKLSITE

BARBARA L. SHERRIFF[§] AND BING ZHOU

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T2N2, Canada

ABSTRACT

Simulations of ²⁹Si and ²³Na MAS NMR spectra indicate the presence of differing proportions of two polytypes and a third phase in three samples of penkvilksite, Na₄Ti₂Si₈O₂₂•5H₂O. The most abundant peaks are assigned to the 2O and 1M polytypes, and a third set of peaks are provisionally assigned to a proposed 2M polytype. The quadrupolar interaction parameters for ²³Na, C_q and η, were calculated using the full-crystal linearized augmented plane-wave model (FC LAPW) for the 1M and 2O polytypes. The values obtained for C_q from the simulations of ²³Na spectra and from the LAPW calculations for the 1M polytype are close, 3.3 and 3.5 MHz, respectively. However, for the 2O polytype, these values are 3.3 and 1.5 MHz, indicating that the Rietveld refinement of the structure for the 2O polytype is not as accurate as the single-crystal refinement of the 1M polytype, from which the 2O structure was optimized to obtain a value of C_q closer to the measured one. The ratios of these polytypes for the three samples of penkvilksite, obtained independently from simulations of ²⁹Si and ²³Na spectra, agree within 9% for the 1M and 2O polytypes.

Keywords: penkvilksite, titanosilicate, ²⁹Si and ²³Na MAS NMR, polytypism, FC LAPW calculations.

SOMMAIRE

Les simulations faites des spectres MAS NMR de ²⁹Si et de ²³Na indiquent la présence de proportions variables de deux polytypes et d'une troisième phase dans trois échantillons de penkvilksite, Na₄Ti₂Si₈O₂₂•5H₂O. Les pics les plus proéminents sont attribués aux polytypes 2O et 1M, et un groupe de pics moins intenses seraient dus à un polytype 2M. Les paramètres C_q et η décrivant l'interaction quadrupolaire du ²³Na dans les polytypes 1M et 2O ont été calculés avec le modèle augmenté linéarisé à onde plane pour cristal complet (FC LAPW). Les valeurs de C_q obtenues pour décrire les spectres simulés de ²³Na et les calculs LAPW effectués pour simuler ceux du polytype 1M sont proches, 3.3 et 3.5 MHz, respectivement. Toutefois, pour le polytype 2O, ces valeurs sont 3.3 et 1.5 MHz; le décalage indique que l'affinement de Rietveld de la structure du polytype 2O ne possède pas la justesse de l'affinement du polytype 1M effectué sur monocristal. Nous avons optimisé la structure du polytype 2O afin d'obtenir une valeur de C_q plus proche de la valeur mesurée. Les proportions de ces polytypes dans les trois échantillons de penkvilksite, telles qu'obtenues de façon indépendante à partir des simulations des spectres de ²⁹Si et de ²³Na pour les polytypes 1M et 2O, concordent à 9% près.

(Traduit par la Rédaction)

Mots-clés: penkvilksite, titanosilicate, spectres MAS NMR de ²⁹Si et de ²³Na, polytypisme, calculs FC LAPW.

INTRODUCTION

Penkvilksite, Na₄Ti₂Si₈O₂₂•5H₂O, is named after its tendency to form curly (*penk*) and white (*vilk*) crystals (Bussen *et al.* 1975). It has been found in the Lovozero alkaline intrusion, Kola Peninsula, Russia (Khomyakov 1995) and at Mont Saint-Hilaire, Canada (Horváth & Gault 1990). Penkvilksite occurs as white clotted concretions up to 7 cm in diameter in cavities with natrolite and radially fibrous aegirine in the Yubileinaya pegma-

tite vein, Mount Karnasurt, Lovozero complex. The concretions are composed of fine-grained aggregates of polygonal platy crystals. Penkvilksite contains about 10 wt% H₂O which, if removed, can be rapidly reabsorbed into the structure, as in zeolites (Khomyakov 1995).

The structure was originally described by Bussen *et al.* (1975), and the unit-cell parameters were revised by Khalilov *et al.* (1977). The structure consists of spiral chains of silicate tetrahedra parallel to the *c* axis joined by TiO₆ octahedra along the *b* axis (Fig. 1). The

[§] E-mail address: bl_sherriff@umanitoba.ca

microporous nature of penkviksite has led to the synthesis of synthetic analogues to investigate their potential for ion-exchange (Lin *et al.* 1997, Liu *et al.* 1997, 1999). Merlino *et al.* (1994) identified four possible maximum degrees of order (MDO) in polytypes of the penkviksite structure, which can be produced from two kinds of layers:

MDO1: $\bar{1}$ at 0 0 and 2_1 parallel to b ($P2_1/c$), penkviksite $1M$

MDO2: $\bar{1}$ at $\frac{1}{4}$ $\frac{1}{4}$ and 2 parallel to b ($I2/c$), penkviksite $2M$

MDO3: n perpendicular to a and 2 parallel to c ($Pnca$), penkviksite $2O$

MDO4: m perpendicular to a and 2_1 parallel to c ($Pmcn$), penkviksite $2O_2$.

They refined the $1M$ polytype in the space group $P2_1/c$ from single-crystal X-ray-diffraction data, and the $2O$ polytype in $Pnca$ using the Rietveld technique with powder X-ray data.

A ^{29}Si MAS NMR spectrum of penkviksite was published by Labouriau *et al.* (1998) in their systematic study of titanosilicate minerals. They allocated the peak at -95.6 ppm to the $\text{Si}(2\text{Si}2\text{Ti})$ and the one at -100.0 ppm to the $\text{Si}(3\text{Si}1\text{Ti})$ environment. However, they failed to identify a third lower-frequency peak in their spectrum.

In this study, three samples of penkviksite were obtained from the Kola Peninsula, and one synthetic sample of $2O$ polytype also was investigated. ^{29}Si MAS NMR spectra were simulated using XEDPLOT (Bruker Ltd.) to obtain values of chemical shift (δ_{iso}) and relative intensities of the peaks. Values of δ_{iso} , C_q and η at the Na site in penkviksite were obtained from simulations of ^{23}Na MAS NMR spectra, and compared with values calculated from the structures of the polytypes using full-crystal linearized augmented plane-wave model (FC LAPW) with the program WIEN2k (Blaha *et al.* 1990, 1992, 2001). The combination of these techniques can provide unequivocal assignment of NMR peaks, and the opportunity to assess structure refinements (Zhou *et al.* 2003, 2004).

BACKGROUND INFORMATION

For nuclei with spin number $I > \frac{1}{2}$, such as ^{23}Na , the non-spherical symmetry of the distribution of nuclear charges produces a nuclear quadrupole moment (Q) (Slichter 1992). The electrostatic interactions between the Q and the electric field gradient (EFG) produce the quadrupolar lineshape, which can contain structural information. The quadrupolar interaction (QI) can be described by the quadrupolar coupling constant (C_q) and

asymmetry parameters (η), which are determined from the EFG at the nuclear site (Slichter 1992):

$$C_q = eV_{zz}Q/h \quad (1)$$

$$\eta = |V_{xx} - V_{yy}| / V_{zz} \quad (2)$$

where V_{zz} , V_{xx} , V_{yy} are the EFG components in Principal Axis System (PAS), e is the electron unit, h is Planck's constant, and Q is the quadrupolar moment, which has a value of 10.0 fm^2 for ^{23}Na (Pyykkö 2001).

In the FC LAPW model calculations, electron exchange and correlation were treated by the density-function theory (DFT) for the complex many-body system of the crystal. The unit cell was partitioned into non-overlapping atomic spheres (centered at an atomic site with a specific radius, R_{mt}) and interstitial regions between the spheres (Blaha *et al.* 1990, 1992, 2001). Different basis-set expansions were used for each of these regions, and the maximum K vector for the basis set is represented by K_{max} . Inside the spheres, the atom-like solutions of Schrödinger's equation (numerical radial functions multiplied by spherical harmonics) were chosen as the basis sets for the crystal-wave functions, whereas plane waves were used as the basis functions in the interstitial regions (Blaha *et al.* 2001, Cottenier 2002). In such a way, the many-body problem of interacting electrons and nuclei was transformed into a series of non-interacting one-electron Kohn-Sham (KS) equations (Kohn & Sham 1965). From these KS equations, the crystal wave-functions were solved, and the electronic structure was obtained using the Rayleigh-Ritz variational principle (Grosso & Parravicini 2000).

EXPERIMENTAL

Materials

Three samples of penkviksite, 3121, 3155 and 3156, come from the Yubileynaya hyperagpaitic pegmatite vein of the Lovozero massif in the Kola Peninsula. All three samples are spheroidal nodules 2 to 4 cm across; 3121 and 3155 consist of loose materials, whereas nodule 3156 consists of compact porcelaneous materials. A synthetic sample of $2O$ polytype was provided by Dr. Stefano Merlino, Dipartimento di Scienze della Terra, Università degli Studi di Pisa, Italy.

NMR spectroscopy

MAS NMR data pertaining to the three natural samples were recorded on the AMX500 instrument with samples spinning at about 8 kHz with a Doty 5 mm MAS probe at the Prairie Regional NMR Centre, Winnipeg, Manitoba. The ^{29}Si spectra were obtained at a frequency of 99.36 MHz, with 2 μs , 30° pulses, recycle delay of 5 s, between 4000 and 9000 free-

induction decays (FID), and referenced to ^{29}Si in tetramethylsilane (TMS). For the ^{23}Na MAS NMR spectra, the frequency used was 132 MHz with a 1 μs pulse, and a recycle time of 0.5 s for the collection of 5000 to 9000 FID. The reference for ^{23}Na was a 1M aqueous solution of NaCl. A range of recycle delays was explored for both ^{29}Si and ^{23}Na to ensure complete relaxation. The spectra of the synthetic *2O* polytype was obtained at Queen's University courtesy of Dr. Gang Wu using a 4-mm MAS probe on a Bruker Avance-500 spectrometer at Queen's University rotating at 12.5 kHz. The ^{29}Si spectrum was acquired at a frequency of 99.3 MHz, with 6 μs pulse length, a 60 s delay and 393 scans. The ^{23}Na spectrum was acquired at a frequency of 132.2 MHz, with a pulse length of 5 μs , and 16 scans with a 5 s delay. References were TMS and 0.1 M solution of aqueous NaCl for ^{29}Si and ^{27}Al , respectively.

The relative intensities of the ^{29}Si peaks were obtained from the computer simulations using XEDPLOT (Bruker Ltd.), a least-squares iterative program. The variable parameters, for nuclei with $I = \frac{1}{2}$, were the isotropic chemical shift and the intensity of each peak. The Gaussian and Lorentzian broadening parameters were allowed to vary iteratively rather than constraining them to be equal for each simulation, as a small amount of disorder in the structure could cause variations in peak widths. Each ^{29}Si spectrum was simulated with six peaks. The ^{23}Na spectra of three natural samples were also simulated using XEDPLOT. For this quadrupolar nucleus, values of η and line broadening were input manually, and the values for C_q , δ_{iso} and relative intensities of the peaks were deduced using a least-squares iterative technique of fitting. The value of η was changed incrementally between simulations until the best match with the experimental spectrum was observed. Each of the ^{23}Na spectra of natural samples of penkviklsite could be simulated with three quadrupolar line shapes, and that of the synthetic *2O* sample, with one. The ^{23}Na spectrum of synthetic *2O* was simulated with program Winfit (Massiot *et al.* 2002). At least three independent fits were done for each ^{29}Si and ^{23}Na spectrum.

TABLE 1. INPUT PARAMETERS FOR FC LAPW CALCULATIONS FOR PENKVIKLSITE USING PROGRAM WIEN2K

Penkviklsite $\text{Na}_x\text{Ti}_y\text{Si}_z\text{O}_{12} \cdot 5\text{H}_2\text{O}$	R_{mt} (a.u.) for each atom in the unit cell	Cut-off $R_{\text{mt}}K_{\text{max}}$	k -points	Number of plane waves used
<i>1M</i> (<i>P21/c</i>)	Ti: 1.75 Si: 1.20 Na: 1.80 O: 1.20 H: 1.00	3.0	128	42496
<i>2O</i> (<i>Pnca</i>)	Ti: 1.75 Si: 1.20 Na: 1.80 O: 1.20 H: 0.90	3.0	128	43382

Note: K_{max} is the maximum K vector for the basis set. R_{mt} is the specific radius of the atomic site.

FC LAPW calculations

The input parameters for the FC LAPW calculations for penkviklsite polytypes *1M* and *2O* are listed in Table 1; the structure data are from Merlino *et al.* (1994). The calculations were run in parallel mode on the High Performance Computing (HPC) facility of the University of Manitoba. These self-consistent field cycles (SCF) were run at the non-spin-polarized mode.

RESULTS AND DISCUSSION

Interpretation of experimental spectra

The ^{29}Si MAS NMR spectra of penkviklsite consist of three separately well-resolved peaks at -95.8 , -100.1 and -101.7 ppm. There is also a small poorly resolved peak at -93.8 ppm and a shoulder at about -97 ppm. The relative intensity of these peaks varies among samples (Fig. 2). Each ^{29}Si spectrum of penkviklsite can be simulated by six peaks (Table 2, Fig. 3). These peaks can be grouped into three pairs of peaks at -101.2 ± 0.1 and -95.9 ± 0.1 ppm, -99.6 ± 0.1 and -95.3 ± 0.1 ppm, and -99.0 ± 0.1 and -93.8 ± 0.1 ppm, with similar intensities within each pair.

The pair with most intense peaks (-99.6 and -95.3 ppm) in all three spectra were assigned to the Si(2) (3Si1Ti) and Si(1)(2Si2Ti) sites of the most common

TABLE 2. ^{29}Si MAS NMR PARAMETERS FOR POLYTYPES OF PENKVIKLSITE AND THE ASSIGNMENT OF THE NMR PEAKS

Specimen		3155	3121	3156
Peak 1	Chemical shift	-101.2 ppm	-101.2 ppm	-101.2 ppm
	Peak width	90 (± 20) Hz	98 (± 20) Hz	65 (± 20) Hz
	Relative intensity	20 (± 5)%	13 (± 5)%	3 (± 1)%
Peak 2	Chemical shift	-99.7 ppm	-99.6 ppm	-99.5 ppm
	Peak width	79 (± 10) Hz	71 (± 10) Hz	59 (± 10) Hz
	Relative intensity	33 (± 5)%	39 (± 5)%	46 (± 5)%
Peak 3	Chemical shift	-98.8 ppm	-99.1 ppm	-99.0 ppm
	Peak width	11 (± 10) Hz	39 (± 10) Hz	38 (± 10) Hz
	Relative intensity	0.3 (± 1)%	1 (± 1)%	1 (± 1)%
Peak 4	Chemical shift	-95.9 ppm	-95.9 ppm	-95.8 ppm
	Peak width	72 (± 10) Hz	68 (± 10) Hz	41 (± 10) Hz
	Relative intensity	17 (± 5)%	10 (± 3)%	2 (± 1)%
Peak 5	Chemical shift	-95.4 ppm	-95.3 ppm	-95.3 ppm
	Peak width	65 (± 10) Hz	58 (± 10) Hz	53 (± 10) Hz
	Relative intensity	26 (± 5)%	31 (± 5)%	41 (± 5)%
Peak 6	Chemical shift	-93.9 ppm	-93.8 ppm	-93.7 ppm
	Peak width	104 (± 20) Hz	100 (± 20) Hz	148 (± 20) Hz
	Relative intensity	4 (± 1)%	5 (± 1)%	6 (± 1)%
<i>2O</i>	Si2(3Si1Ti) <Si-O> 1.627 Å	-99.7 ppm	-99.6 ppm	-99.5 ppm
	Si1(2Si2Ti) <Si-O> 1.630 Å	-95.4 ppm	-95.3 ppm	-95.3 ppm
<i>1M</i>	Si2(3Si1Ti) <Si-O> 1.619 Å	-101.2 ppm	-101.2 ppm	-101.2 ppm
	Si1(2Si2Ti) <Si-O> 1.629 Å	-95.9 ppm	-95.9 ppm	-95.8 ppm
Third phase	Si2(3Si1Ti) <Si-O> *1.631 Å	-98.8 ppm	-99.1 ppm	-99.0 ppm
	Si2(3Si1Ti) <Si-O> *1.634 Å	-93.9 ppm	-93.8 ppm	-93.7 ppm
	Si1(2Si2Ti) <Si-O> *1.634 Å	-93.9 ppm	-93.8 ppm	-93.7 ppm

* calculated from the ^{29}Si MAS NMR data of the *2O* and *1M* polytypes.

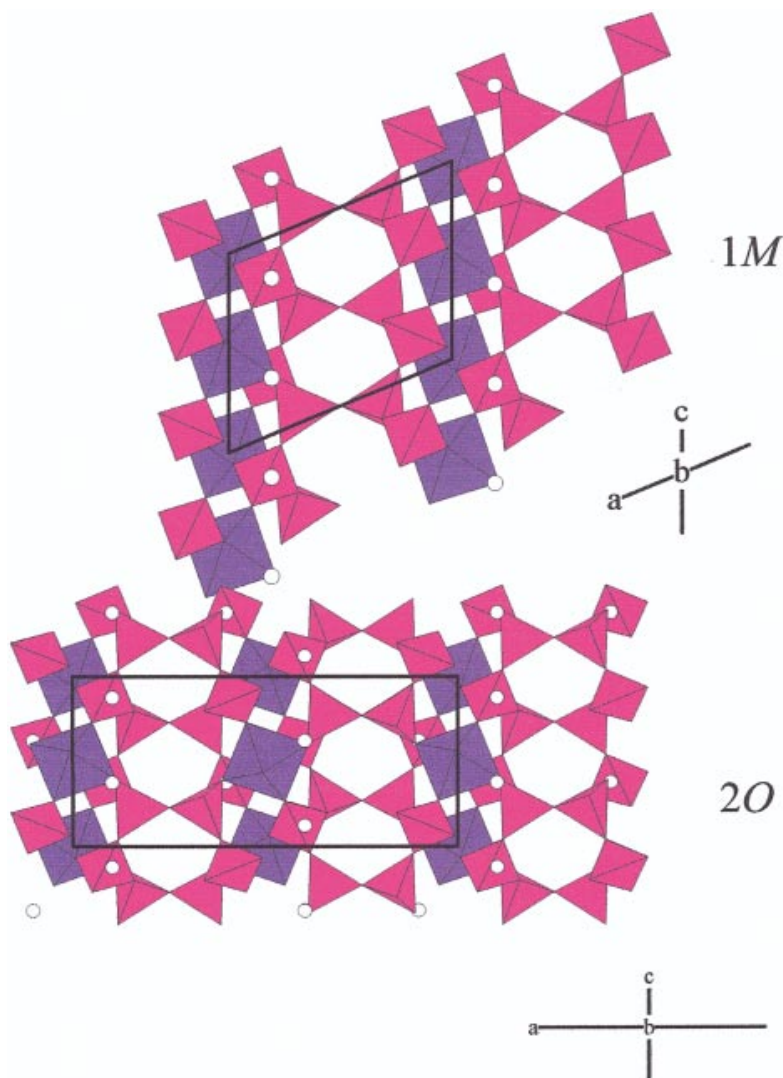


FIG. 1. The structure of penkvilksite polytypes *2O* and *1M* (Merlino *et al.* 1994). The unit cells are delineated in black. The Ti octahedra are shown in purple, and the Si tetrahedra, in magenta. Open circles: Na polyhedra.

2O polytype by Labouriau *et al.* (1998), with $\langle\text{Si-O}\rangle$ bond lengths of 1.627 and 1.630 Å, respectively (Merlino *et al.* 1994). The $\langle\text{Si-O}\rangle$ distances for the *1M* polytype were found by Merlino *et al.* (1994) to be 1.619 and 1.629 Å. The ^{29}Si spectrum of the *1M* polytype would be expected to be similar to that of the *2O* polytype with two peaks of equal intensity. The ^{29}Si peaks tend to move to higher frequency with reduced Si-O distance (Sherriff *et al.* 1991). Therefore, the Si(1)(2Si2Ti) peak of the *1M* polytype would be expected to be shifted by at least 1 ppm to a higher fre-

quency compared with that of the *2O* polytype, whereas the Si(2)(3Si1Ti) peak of *1M* should be shifted only slightly from the position for the corresponding *2O* peak, owing to the smaller difference in bond distance for Si(2) compared to Si(1) between the polytypes.

Thus, the peaks at -101.2 ppm and -95.9 ppm were assigned to the Si(2)(3Si1Ti) and Si(1)(2Si2Ti) site in *1M*, respectively. The remaining two small peaks at -98.8 and -93.9 ppm were provisionally assigned to the Si(2)(3Si1Ti) and Si(1)(2Si2Ti) sites of a possible third polytype, which would be expected to have a $\langle\text{Si(2)-}$

O> distance of 1.631 Å and a <Si(1)–O> distance of 1.634 Å. The relative intensities, positions and widths of these small peaks have a much higher uncertainty than the major peaks because of the low signal-to-noise ratio.

The ^{23}Na MAS NMR spectrum of the synthetic 2O polytype of penkvilksite (Fig. 4) consists of a quadrupolar lineshape, which can be simulated using values of C_q of 3.30 MHz, η of 0.45 and δ_{iso} of 4.3 ppm (Fig. 5). The ^{23}Na spectrum of sample 3156 is very similar to that of synthetic 2O polytype (Fig. 4), but the spectra of samples 3155 and 3121 have extra peaks in the center of the quadrupolar doublet at about -2 and -6 ppm (Fig. 4), respectively. Each ^{23}Na spectrum of the penkvilksite samples from Kola can be simulated by three quadrupolar lineshapes with a value of η of 0.45, and 1320 Hz line broadening (Fig. 5). The most intense peak in each spectrum has a δ_{iso} of 4.6 ± 0.2 ppm and a C_q of 3.30 ± 0.01 MHz. The next most intense peak has δ_{iso} of 6.5 ± 0.4 ppm and C_q of 3.14 ± 0.03 MHz, and the least intense peak has values of δ_{iso} of 11.5 ± 2 ppm and C_q of

3.24 ± 0.2 MHz (Table 3). The most intense peak, which has the lowest frequency δ_{iso} of 4.6 ppm, is assigned to the Na site in the 2O polytype, in agreement with the simulation made for the synthetic 2O polytype. The next most abundant peak, at 6.5 ppm, is assigned to the 1M polytype. The similarity between the C_q values of the third phase and of the 2O polytype indicates similar symmetry, but the higher-frequency δ_{iso} points to a site with less shielding. The third phase found by NMR is possibly the 2M polytype (MDO2), as Merlino *et al.* (1994) found that the O–O distances in the MDO2 polytype were too close for the structure to be stable.

FC LAPW calculations

The FC LAPW model has been shown to be the most accurate method for calculating the electric density and EFG in an ordered crystal at this time (Bryant *et al.* 1999, Zhou & Sherriff 2004). The calculations using the FC LAPW model with WIEN2k gave the C_q and η values 3.54 MHz and 0.48 for ^{23}Na in the 1M polytype,

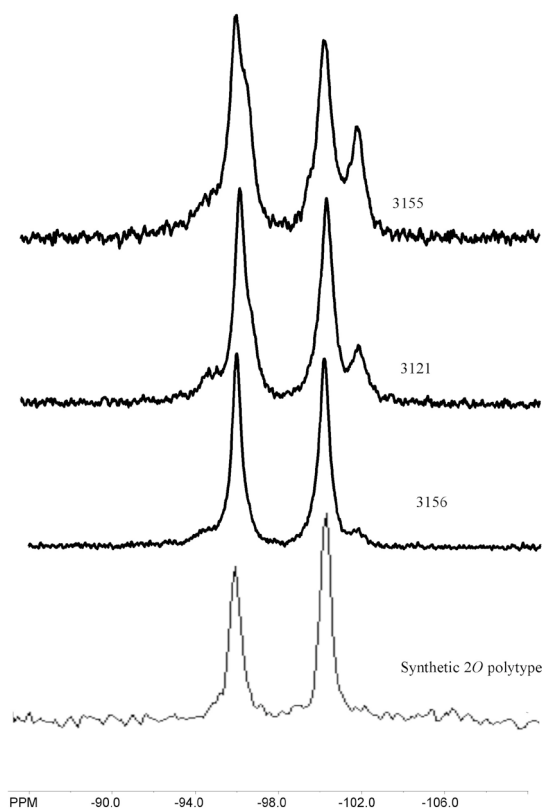


FIG. 2. The ^{29}Si MAS NMR spectra of natural samples 3155, 3121, 3156 and the synthetic 2O polytype of penkvilksite.

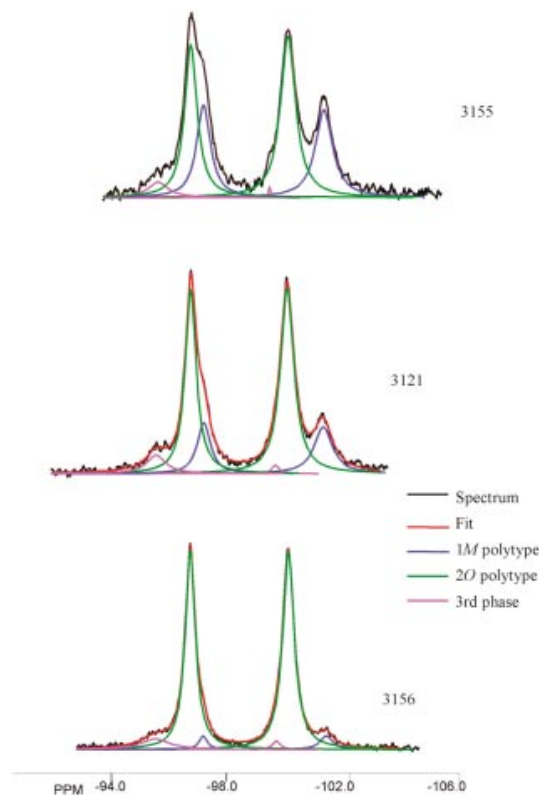


FIG. 3. The simulated ^{29}Si MAS NMR spectra samples 3155, 3121 and 3156. The parameters of the simulated spectra are given in Table 2.

and 1.53 MHz and 0.79 in 2O polytype, respectively (Table 3). The negative calculated values for V_{zz} indicate a prolate shape for the electric distribution around the Na site. The calculated results for polytype 1M using the FC LAPW method are thus in good agreement with the experimental values, but there is a large discrepancy between the theoretically calculated C_q using WIEN2k and the experimental C_q value for polytype 2O. The value of 3.3 MHz for the experimental value is constrained by the spectrum of the synthetic sample, which has a width exceeding 3 MHz. Some problems were encountered in the Rietveld structure refinement by Merlino *et al.* (1994). The sample of polytype 2O used for the refinement was found to be intergrown with a small amount of the 1M polytype, which produced additional and in some cases overlapping XRD peaks. There was also a possibility of disorder caused by Zr in the Ti site. Therefore, we feel that the value of 3.3 MHz obtained from the simulation of the spectra is correct, and the low value of 1.5 MHz derived from the calculations is due to inaccuracies in the structure refinement. However, owing to the sensitivity of the EFG calculations using the FC LAPW model to the atom coordinates, the structure of polytype 2O can be optimized by

adjusting the atom coordinates in the unit cell until the minimum atomic forces were reached using WIEN2k. The EFG from such an optimized polytype 2O structure gave C_q value of 2.97 MHz at the Na site, which is much closer to the experimental result.

The ratios of the polytypes obtained independently from simulations of ^{29}Si and ^{23}Na spectra agree within 9% for the polytypes 2O and 1M for all three samples of penkviksite (Table 4). Variations for values for the third phase are due to the low signal-to-noise ratio, leading to large uncertainties in the fitting procedure. This agreement validates the assignment of the major peaks to the two polytypes, 2O and 1M.

Correlation between ^{23}Na parameters and structure

Koller *et al.* (1994) developed an empirical correlation between bond valences (Brown & Shannon 1973) and δ_{iso} for ^{23}Na in a series of sodium compounds. Bond valences using seven oxygen atoms in a sphere within 3 Å around the central Na in polytypes 1M and 2O were calculated using equation 3 (Brown & Altermatt 1985):

$$s_{ij} = e^{(r_0 - r_{ij})/B} \quad (3)$$

TABLE 3. ^{23}Na MAS NMR PARAMETERS OF PENKVIKSITE PHASES AND THE CALCULATED QI PARAMETERS USING FC LAPW AND BOND-VALENCE MODELS

Sample	phases	δ_{iso} ppm	η	C_q MHz	Relative intensity
3121	phase 1	4.4	0.45	3.30	74 (± 5)%
	phase 2	6.1	0.45	3.18	15 (± 5)%
	phase 3	9.7	0.45	3.24	11 (± 1)%
3155	phase 1	4.9	0.45	3.33	52 (± 5)%
	phase 2	6.4	0.45	3.16	28 (± 5)%
	phase 3	9.9	0.45	3.15	21 (± 5)%
3156	phase 1	4.5	0.45	3.29	81 (± 5)%
	phase 2	6.8	0.45	3.07	11 (± 3)%
	phase 3	13.1	0.45	3.36	8 (± 1)%
Synthetic	2O	4.3	0.45	3.30	100 %
Calculated QI values					
FC LAPW model	1M		0.48	3.54	
	2O		0.79	1.53	
Bond-valence model	1M	-32.3	0.07	1.72	
	2O	-30.4	0.37	1.19	

TABLE 4. THE PROPORTION OF PENKVIKSITE PHASES CALCULATED FROM SIMULATED NMR DATA

Phase		3155	3121	3156
2O	^{29}Si	59%	70%	87%
	^{23}Na	52%	74%	81%
1M	^{29}Si	37%	23%	5%
	^{23}Na	28%	17%	11%
3 rd phase	^{29}Si	4%	6%	7%
	^{23}Na	21%	9%	8%

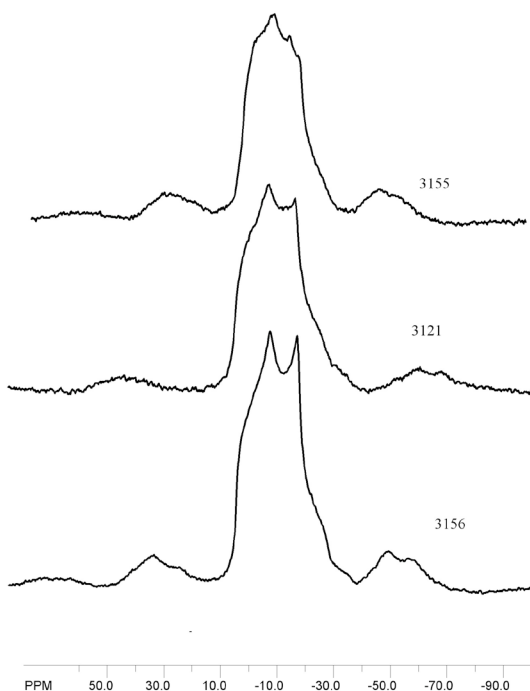


FIG. 4. The ^{23}Na MAS NMR spectra of natural samples 3155, 3121 and 3156.

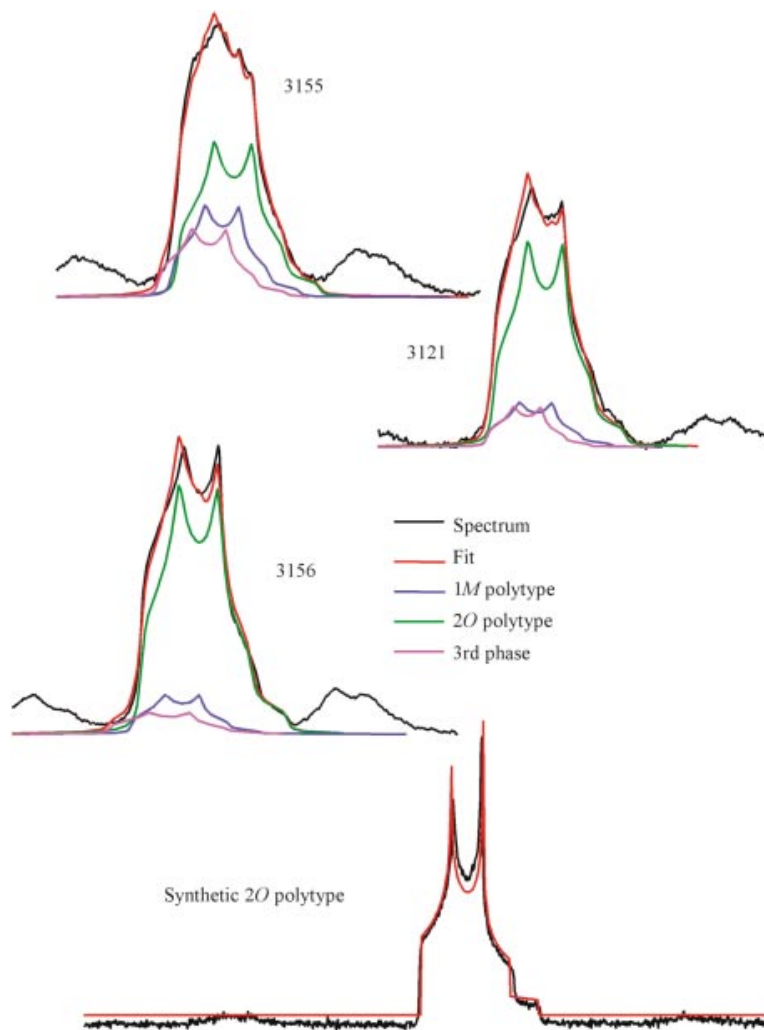


FIG. 5. The simulated ^{23}Na MAS NMR spectra of natural samples 3155, 3121, 3156 and the synthetic $2O$ polytype of penkvilksite. The parameters of the simulated spectra are given in Table 3.

where r_0 is the ideal bond-length between the O atom i and its nearest-neighbor cation j , r_{ij} is the measured bond-distance between atoms i and j , and B is an empirical constant (0.37). Correspondingly, the chemical shifts of ^{23}Na in the $2O$ and $1M$ polytypes of penkvilksite, calculated from these bond valences using the empirical relationship of Koller *et al.* (1994), gave values of -30.4 and -32.3 ppm, respectively, which are far from the experimental results of 4.4 and 6.1 ppm.

Bond valence (s_{ij}) could also be used to calculate the EFG at the Na site, and thus C_q and η for ^{23}Na from the effective charge q_i obtained by using equation 4 for O atom (i) around the Na atom (Koller *et al.* 1994)

$$q_i = \left(\sum_j a s_{ij}^M \right) - 2 \quad (4)$$

where a and M are the empirical constants determined by the number of core electrons of the cation j bonded to the O atom i (Brown & Shannon 1973). From the coordinates and charges calculated for the seven O atoms around the Na atom using the program FG (H. Koller, pers. commun.), values of 1.72 MHz and 0.07 were derived for C_q and η of the ^{23}Na for the $1M$ polytype, and 1.18 MHz and 0.37 for $2M$. These results

are about a factor of two lower than the experimental ones.

George & Stebbins (1995) found a similar discrepancy between the experimental and predicted δ_{iso} for ^{23}Na in silicates and concluded that the empirical model of Koller *et al.* (1994) is not valid for silicate structures. The high electron-density of Ti could also have caused discrepancies in the model of Koller *et al.* (1994).

Xue & Stebbins (1993) found ^{23}Na δ_{iso} of silicate crystalline structures, melts and glasses also to be affected significantly by the network modifiers around Na and number of non-bridging O per tetrahedron (NBO/T). Using a NBO/T value of 1.5, an average bond-length of 2.5 Å for the <Na–O> bond, and the correlation diagrams of Xue & Stebbins (1993), δ_{iso} values were estimated for the seven-coordinated ^{23}Na in both 1M and 2O polytypes of penkvilksite. The results, between 8 and 10 ppm, are close to the experimental results of 4.4, 6.4 and 9.7 ppm for the three phases. Generally, the δ_{iso} of ^{23}Na decreases with increasing coordination-number (Dirken *et al.* 1992), but other factors such as the type of modifier cations also play an important role. The presence of the high-field-strength Ti as the first cation neighbor causes a high electron-density around Na, resulting in a higher-frequency δ_{iso} for ^{23}Na in penkvilksite.

CONCLUSIONS

Simulations of the MAS NMR spectra of three different samples of penkvilksite from the Kola Peninsula and a synthetic sample of the 2O polytype allowed the identification and evaluation of ^{29}Si and ^{23}Na peaks relating to three separate phases in the minerals. Two of these were identified as the 2O and 1M polytypes, and the third phase is tentatively assigned to a 2M polytype. The proportion of these polytypes varies among the different natural samples of penkvilksite. The QI parameters calculated from refined structures using FC LAPW agree closely with the experimental data for 1M, but not for the 2O polytype, indicating that there may be inaccuracies in the structure refinement of this polytype, which can be optimized using FC LAPW calculations.

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