

Crystal chemistry of narsarsukite

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Abstract : The finding of Zr-rich narsarsukite in a peralkaline lava from Morocco prompted a re-evaluation of the crystal chemistry of this mineral. Microprobe analyses show that F is present in narsarsukite from all known occurrences. An examination of two specimens (from Narsarsuk and Montana) by Mössbauer spectroscopy indicates that most of the iron is present in the trivalent state. The infrared spectra of three specimens exhibit four absorption bands in the 4000-3000 cm⁻¹ range. The assignment of these bands either to hydroxyls or water molecules is discussed, the latter hypothesis being favoured. Significantly larger unit-cell parameters in the Moroccan sample are compatible with the extensive replacement of Ti by Zr. The entry of F in the structure is coupled with the replacement of Ti by Fe³⁺, F substituting the underbonded apical oxygens of the TiO₆ octahedra. These new results suggest that the general formula Na₂ [(Ti,Zr)_(1-x)Fe_x³⁺] O_{(1-x)F_x}Si₄O₁₀·(0-1/2)H₂O, with 0 ≤ x ≤ 1, may be proposed for narsarsukite.

Key-words : narsarsukite (Zr-bearing), Mössbauer, FTIR, crystal chemistry, Sirwa Massif (Morocco).

Introduction

The structure of narsarsukite, unusual for a silicate, is made up of Si₄O₁₀ chains which form tubes of rings of four tetrahedra, parallel to the *c* axis. These tubes are linked by chains of corner-sharing Ti-octahedra, also running parallel to the *c* axis (Pyatenko & Pudovkina, 1960 ; Peacor & Buerger, 1962). Na atoms are situated in cavities between Si₄O₁₀ tubes and octahedral chains.

Gössner & Strunz (1932) proposed the formula Na₂TiSi₄O₁₁ with four formula units per cell for narsarsukite from the type locality Narsarsuk, Greenland. They noticed the possible partial isomorphic substitution with a Na₂Fe³⁺Si₄O₁₀F component and supposed also the existence of a third component Na₂M²⁺Si₄O₉F₂ to explain the presence of small amounts of Mg and Mn. Warren & Amberg (1934) proposed a similar formula Na₂(Ti,Fe)Si₄O₁₁ without considering the presence of OH and F. Since two oxygen atoms

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are linked to Ti atoms only, the formula may be more explicit when written as $\text{Na}_2\text{TiOSi}_4\text{O}_{10}$ (Peacor & Buerger, 1962) or as $\text{Na}_2(\text{Ti,Fe})\text{Si}_4\text{O}_{10}(\text{O,OH,F})$ taking into account OH and F (Vlasov *et al.*, 1966).

The purpose of this note is first to report the high Zr content of narsarsukite from a peralkaline rock (comendite) from Morocco, then to show the ubiquitous occurrence of F and Fe^{3+} in this mineral and last to discuss the presence in it of hydroxyls and/or water molecules. Specimens were obtained from Sage Creek, Montana; Mont Saint-Hilaire, Quebec (no. P41858, Musée de l'École des Mines de Paris); Gouré, Damagaram, Niger (no. T128, Museum National d'Histoire Naturelle, Paris); Narsarsuk, Greenland (no. 100-793, Museum National d'Histoire Naturelle, Paris; no. L26368, Musée de l'École des Mines de Paris; no. 21739, Museo Mineralogica dell' Università di Roma).

Experimental methods

Narsarsukite analyses were performed on a CAMEBAX automated electron microprobe. Experimental conditions were the following: acceleration voltage, 15 kV; current intensity, 10 nA; counting time, 10 s; standards were oxides or natural minerals. Fluorine was determined using the F $K\alpha$ peak with a TAP crystal. Standardizations were made regularly by analyzing a F-phlogopite standard, and the analyses reported below were all from the same batch. Moreover, no fluorine was detected on F-free mineral standards. Precision was estimated at the 95 % confidence level for each element ($2\sigma = 1\%$ for Si, 3 % for Na, 2-3 % for Ti, 6-9 % for Fe, 4 % for Zr and 25 % for F).

The X-ray powder diffraction patterns were obtained by means of a Gandolfi camera using Ni-filtered $\text{Cu}K\alpha$ radiation ($\lambda = 1.5418\text{\AA}$). Exposure times were 96 hours. Owing to the lack of single-crystal data, indexing was made by comparison with the JCPDS card no. 11-478, and least-squares refinement of the unit-cell parameters was performed with the computer program LSQ82 (Hubbard *et al.*, 1982).

Infrared spectra were obtained using a Nicolet 5DX FTIR spectrometer with a dried air beam path, DTGS detector and KBr window. Samples were dried overnight at 115°C and prepared as KBr pellets ($\varnothing = 6\text{ mm}$, 1 mm thickness) with a concentration of less than 1 wt% silicate in the sample.

Two samples were available in amounts sufficient for Mössbauer analysis. The samples were ground under acetone in an agate mortar. For the Narsarsuk L26368 sample, a split of 100 mg was mixed with the same amount of sucrose and pressed as a 1 cm diameter pellet. Only 15 mg of the Montana sample, however, were available; the powder was directly loaded into a 2.5 mm diameter bore in a lead disk. Both samples had a spectral thickness of about 3 mg/cm² of natural Fe. Spectra were accumulated at room temperature, in a 1024-channel PROMEDA-ELSCINT analyzer utilizing the symmetrical acceleration mode and a 3mCi $^{57}\text{Co/Rh}$ source. Long accumulation times (140 and 464 hours) were required because of the small overall absorption effect (maximum 2.4 % of the baseline compared to a usual 5 to 10 %), the relatively large X-ray absorption and the small weight of the Montana sample. Folded spectra were fitted to Lorentzian lines, using a program developed at the laboratory. Pure Fe foil spectra were used for calibration, following the recommended values given by Dyar (1984).

Previous data on narsarsukite

The narsarsukite from the type locality, Narsarsuk, contains 0.71 wt% F and 0.29 wt% H_2O (Christensen, in Flink, 1901). A specimen from Halbbreed Creek, Montana, is richer in Ti and poorer in Fe than the Narsarsuk material but does not contain any F (Graham, 1935). Upton *et al.* (1976) analyzed separated crystals of poikilitic narsarsukite from another occurrence in South Greenland and found 0.73 wt% F but no H_2O . Two electron-microprobe analyses of a narsarsukite from East Greenland (Brooks *et al.*, 1982) have low sums (95.76-96.97 %), but F was not analyzed. Narsarsukite specimens from other occurrences: Quebec (Rajasekaran, 1966), Niger (Jérémine & Christophe Michel-Lévy, 1961; Black, 1963) and Kola peninsula (Vlasov *et al.*, 1966), contain numerous inclusions; recalculated analyses give only poor informations but show no H_2O .

These disparate data prompted us to reexamine narsarsukite from different localities. Representative analyses are given in Table 1, and a list of all analyses is available upon request.

Table 1. Representative microprobe analyses of narsarsukite.

	Morocco		Montana	Quebec	Niger	Narsarsuk			L26638
						100-793	21739		
SiO ₂	60.85	60.78	62.50	63.05	61.37	62.21	61.69	63.74	61.31
Al ₂ O ₃	0.63	0.79	0.16	0.59	0.64	0.90	0.82	0.53	0.56
Fe ₂ O ₃	2.92	3.14	2.29	4.10	5.88	6.57	6.53	5.55	6.05
MgO	0.17	0.11	0.16	0.07	-	0.04	-	-	-
MnO	1.04	1.18	-	0.06	-	0.22	0.27	0.20	0.17
TiO ₂	9.97	9.88	17.03	14.55	12.15	11.57	11.54	13.74	11.87
ZrO ₂	5.41	5.67	0.37	0.30	0.91	-	-	0.64	0.91
Na ₂ O	13.54	14.81	14.72	16.91	15.41	15.97	16.07	15.48	15.97
K ₂ O	0.75	0.74	0.38	0.16	0.20	-	-	0.13	-
F	0.87	1.42	0.59	1.53	1.51	2.14	1.64	1.38	1.28
O=F	0.37	0.60	0.25	0.64	0.64	0.90	0.69	0.58	0.54
Total	95.78	97.92	97.95	100.68	97.43	98.72	97.87	100.81	97.58
Structural formulae : 7-cation basis									
Si	4.165	4.048	4.102	3.973	4.043	4.027	4.012	4.073	4.011
Al	0.051	0.062	0.012	0.044	0.050	0.069	0.063	0.040	0.043
Fe ³⁺	0.150	0.157	0.113	0.194	0.291	0.320	0.320	0.267	0.298
Mg	0.017	0.011	0.016	0.007	-	0.004	-	-	-
Mn	0.060	0.066	-	0.003	-	0.012	0.015	0.011	0.009
Ti	0.513	0.495	0.841	0.690	0.602	0.563	0.564	0.660	0.584
Zr	0.181	0.184	0.012	0.009	0.029	-	-	0.020	0.029
Na	1.797	1.913	1.873	2.067	1.968	2.005	2.026	1.918	2.026
K	0.065	0.063	0.032	0.013	0.017	-	-	0.011	-
F	0.188	0.299	0.122	0.305	0.315	0.438	0.337	0.279	0.265

Zr-bearing narsarsukite from Morocco

Occurrence

The narsarsukite was found in a comendite, an oversaturated peralkaline rock (MacDonald, 1974) from the Sirwa Massif, a 25 km-diameter Miocene to Quaternary volcano situated North of the town of Ouarzazate, in Southern Morocco. The comendite neck is located at Tazoult ($x = 291.7$ and $y = 420.4$, Tachoukacht sheet of the Morocco 1 : 50000 topographical map). The comendite rock has been dated at 5.6 Ma by the K/Ar method (M. Delafoye, Laboratoire de Géochronologie, Genève, pers. comm.).

Narsarsukite occurs as rare, small (60 x 80 μm), colourless, inclusion-free crystals in the groundmass of the comendite. It coexists with alkali feldspar, arfvedsonite and aegirine. The bulk chemical analysis of the rock shows a high Zr content of 2700 ± 50 ppm (Table 2). Although concentrated in narsarsukite, ZrO₂ exceeds 1 wt% in clinopyroxene; amphibole is almost Zr-free.

Cell dimensions

The X-ray diffraction pattern obtained for this Zr-bearing narsarsukite could be indexed in space group $I4/m$ and is consistent with previous data (Stewart, 1959; Rajasekaran, 1966). Cell dimensions refined using 12 reflections in the range $16-71^\circ 2\theta$ are reported in Table 3 and compared to other data; they appear to be larger in the Moroccan narsarsukite, possibly as the ionic radius of six-fold coordinated Zr⁴⁺ (0.72 Å) is significantly larger than that of Ti⁴⁺ (0.605 Å; Shannon, 1976).

Chemical composition

The main characteristic of the Moroccan narsarsukite is the high zirconium content (up to 5.7 wt% ZrO₂), associated with low TiO₂ values. This significant replacement of Ti by Zr was not reported before. This narsarsukite contains iron and manganese (around 3 wt% Fe₂O₃ and 1 wt% MnO). The F content ranges from 0.8 ± 0.2 to 1.4 ± 0.4 wt%. Even though chemical elements heavier than F besides those

reported (Table 1) are not present in significant amounts, the microprobe analyses show low totals.

Table 2. Bulk chemical composition (X-ray fluorescence analysis) and CIPW norm of the Sirwa comendite (specimen MM 43-83).

SiO ₂ (wt.%)	68.66		
Al ₂ O ₃	14.48		
Fe ₂ O ₃	3.28	Qz	13.21
FeO	0.44	Or	28.31
MgO	0.24	Ab	47.81
MnO	0.15	Ac	6.93
TiO ₂	0.45	Di	1.06
CaO	0.30	Hy	0.11
Na ₂ O	6.58	He	0.47
K ₂ O	4.79	Mt	0.60
P ₂ O ₅	0.02	Il	0.85
H ₂ O	1.00	Ap	0.05
Total	100.39		
Zr (ppm)	2700±50		

Table 3. Cell dimensions of narsarsukite samples.

	a (Å)	c (Å)	V (Å ³)
1	10.76	7.92	917
2	10.72 (0)	7.94 (8)	913
3	10.608	7.984	898
4	10.76 (1)	7.99 (1)	926 (2)

1- Narsarsuk, Greenland in Stewart (1959)
 2- Sage Creek, Montana (Stewart, 1959)
 3- Mont St Hilaire, Quebec (Rajasekaran, 1966)
 4- Sirwa, Morocco (this work)

Presence of F and Fe³⁺

Narsarsukites from Montana and Quebec are the richest in Ti and correlatively the poorest in Zr and Fe. The analyses indicate F contents varying between 0.6 and 2 wt% suggesting that the almost ubiquitous analytical deficit could be, at least in part, due to the presence of hydroxyl groups or water molecules in the structure (see next section).

Mössbauer spectra

A good quality spectrum could only be obtained for the Narsarsuk L26368 specimen

(Fig. 1a). Visually, the spectrum consists of a single prominent absorption peak with a high-velocity shoulder. Fitting of the spectrum with two Lorentzian absorption peaks yields a χ^2 value of 0.95 and structureless residuals (Fig. 1a, bottom) indicating a good fit. Fits of the spectrum to multiple lines either did not converge or gave no statistical improvements. The high-intensity narrow line (peak 2 of Table 4), representing about 25 % of the total absorption, has a line-width in the range observed for Fe³⁺-bearing silicates and oxides. Quadrupole splitting (QS) is therefore likely to be less than 0.2 mm/s, the value of the half-width of the fitted line. Even though the shoulder to peak 2 has been fitted to an unsplit Lorentzian (peak 1 of Table 4), the difference spectrum (Fig. 1b) obtained by subtracting the computed peak 2 from the observed spectrum indicates that the very broad peak 1 may in fact represent the superposition of several doublets of increasing QS and decreasing intensity. Peak 1 yields Mössbauer parameters (Table 4) compatible with Fe³⁺ in an octahedral environment (Bancroft, 1973). Peak 2 is characterized by an isomer shift (IS) near 0 mm/s and a very small (if not zero) QS, values seldom encountered in natural silicates and oxides. The absence of significant absorption from Fe²⁺ may be judged from the spectrum obtained by subtracting peak 1 (Table 4) from the observed spectrum (Fig. 1c).

Narsarsukite from Montana could not be obtained in sufficient amounts to run a good quality spectrum. Only qualitative results can therefore be obtained. The spectrum was fitted to two Lorentzian lines constrained to have the same Mössbauer parameters as sample L26368. Noteworthy is the much reduced narrow-peak absorption effect (Table 4) suggesting again the predominance of Fe³⁺ in octahedral sites.

Discussion

Taking into account Mössbauer results, structural formulae were computed assuming total iron as Fe³⁺. The main difference

Fig. 1. Mössbauer spectrum of narsarsukite from Narsarsuk (L26368).

a) observed spectrum and residuals.

b) difference spectrum obtained by subtracting a single narrow Lorentzian line (peak 2 of Table 4) from a).

c) difference spectrum between a) and peak 1 of Table 4 showing no component attributable to Fe²⁺.

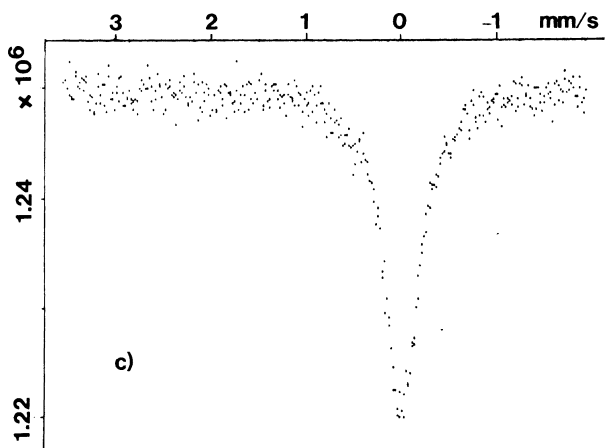
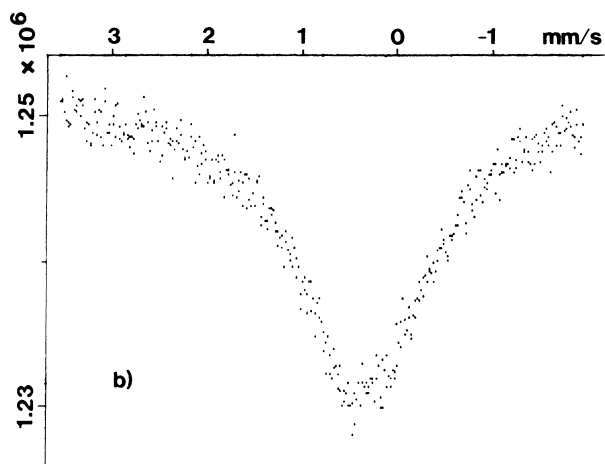
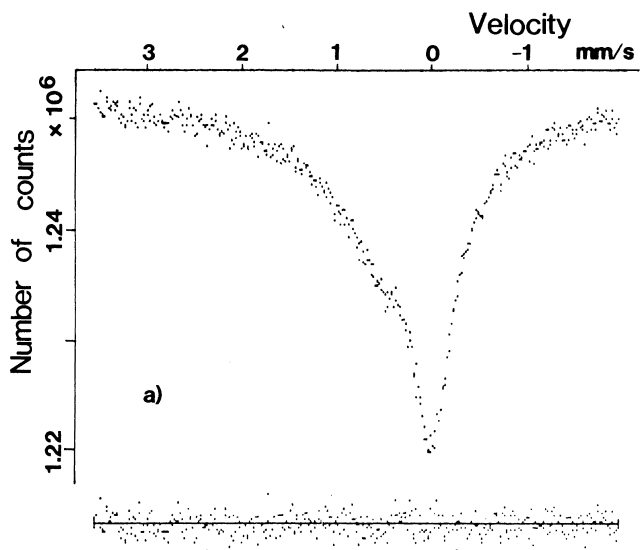


Table 4. Mössbauer parameters for narsarsukite from Narsarsuk (L26368) and Montana given with respect to a Fe-metal calibration ; all values in mm/s.

Sample	Weight mg	Spectral thickness mg nat. Fe/cm ²		Accumulation time h : mn		Base-line counts
L26368	94.9	3.0		140 : 18		1,250,000
Montana	12	3.2		464 : 29		213,000
Sample		IS	QS	FWHM (1)	Intensity (2)	Absorption (3)
L26368	Peak 1	0.427	=0	1.70	1.8	74.2
	Peak 2	0.033	=0	0.44	2.4	25.8
Montana	Peak 1	nd(4)	nd	nd	0.6	91
	Peak 2	nd	nd	nd	0.2	9

1) Full Width at Half Maximum of pure Lorentzian component peaks.
 2) Intensity in % of the base-line counts.
 3) % Absorption is computed from the Intensity x FWHM product.
 Uncertainty is estimated at 5% rel. for sample L26368
 and at not better than 10% rel. for the Montana sample.
 4) nd (not determined); the values obtained for the L26368 sample were used in the fit.

between the Moroccan narsarsukite and those previously described rests in its Zr content (Fig. 2). Fig. 3 represents the variations of Ti + Zr as a function of Fe³⁺ in all analyzed narsarsukites. The relationship is clear and is compatible with a substitution of Ti by Zr, as well as Ti (or Zr) by Fe³⁺. The observed trend lies below the one-to-one correlation, indicating the probable contribution of Al³⁺ and M²⁺ (for example Mn in the Moroccan narsarsukite). The F vs Fe³⁺ diagram (Fig. 4) shows a good correlation between the two variables with an equation $F = 1.03 \text{ Fe}^{3+} + 0.02$.

The observed relation between Fe³⁺ and F can be explained. Ti (+Zr) being substituted by Fe³⁺ (+Al³⁺), the charge balance must be maintained by a correlative decrease of the negative charges, a change accomplished by proxying F for the apical oxygens of the octahedral chain, leading to the general formula : $\text{Na}_2[(\text{Ti}, \text{Zr})_{(1-x)}\text{Fe}_x^{3+}] \text{O}_{(1-x)}\text{F}_x\text{Si}_4\text{O}_{10}$. This formula is valid for $0 \leq x \leq 1$ with two possible end members : $\text{Na}_2(\text{Ti}, \text{Zr})\text{OSi}_4\text{O}_{10}$ and $\text{Na}_2\text{Fe}^{3+}\text{FSi}_4\text{O}_{10}$, which are consistent with the propositions of Gössner & Strunz (1932). Even though iron is present mostly in the ferric state, biva-

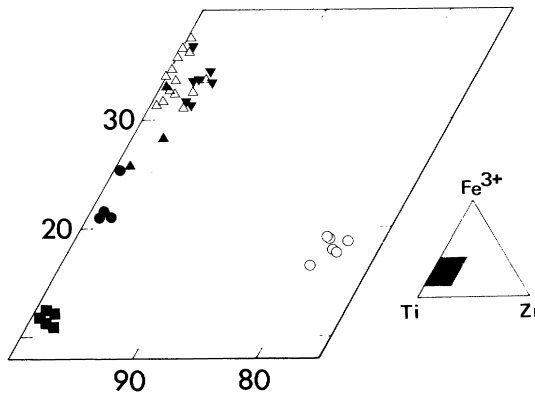


Fig. 2. Composition of narsarsukites in a Fe³⁺-Ti-Zr diagram (atomic percent). Narsarsukites from Morocco (open circles), Montana (solid squares), Gouré (solid triangles, apex down), Quebec (solid circles) and Narsarsuk (open triangles, specimens 100-793 and L26368 ; solid triangles, apex up, specimen 21739).

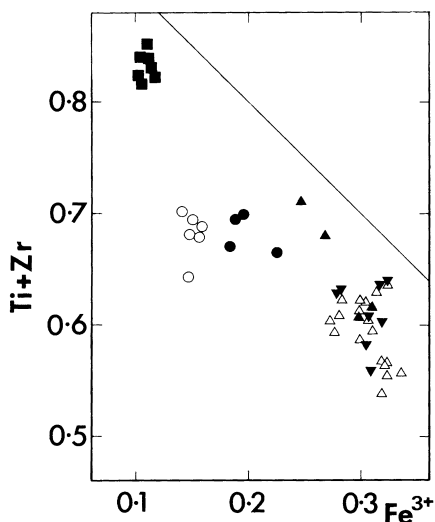


Fig. 3. Distribution of (Ti + Zr) and Fe^{3+} (atomic per cent) in narsarsukites. Symbols as in Fig. 2. The solid line refers to the 1 : 1 correlation.

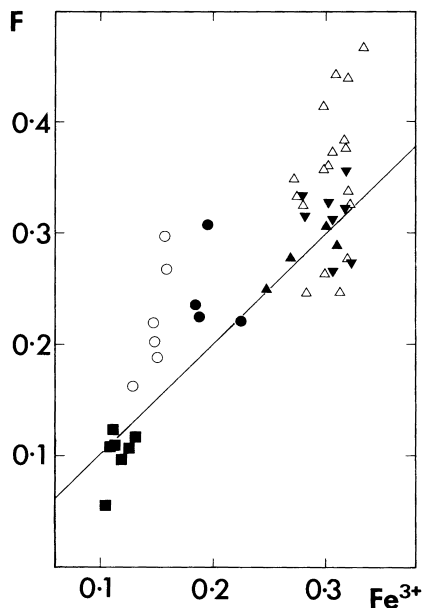


Fig. 4. Distribution of F and Fe^{3+} (atomic per cent) in narsarsukites. Symbols as in Fig. 2. The solid line refers to the 1 : 1 correlation.

lent cations may also be involved in the substitution according to: $\text{Na}_2[(\text{Ti}, \text{Zr})_{(1-x)}\text{M}_x^{2+}] \text{Si}_4\text{O}_{10}\text{O}_{(1-2x)}\text{F}_{2x}$, with $0 \leq x \leq 0.5$; this scheme implying 2F for each proxying M^{2+} . The slope

of the F vs Fe^{3+} diagram (Fig. 4) confirms that the first mechanism is predominant. The excess of F relative to the one-to-one correlation for some samples is related to the contribution of M^{2+} cations. The most adequate solution, consistent with both the local charge balance and with the proposed substitution, is to consider a succession of $\text{Fe}^{3+}\text{-F-Ti}^{4+}$ in the octahedral chains. We may suppose that the substitution of Ti by Fe^{3+} diminishes the bond-valence exchanged with the apical oxygens of the octahedra enough to allow the introduction of F in the structure. This local ordering may well occur, in particular in specimen 21739 from Narsarsuk in which the numbers of Fe^{3+} and F atoms are similar (0.27 and 0.28 atoms p.f.u., respectively).

Presence of hydroxyls or water molecules

Infrared spectra

Infrared spectra were performed on the specimens that showed low oxide sums (except no. 21739 from Narsarsuk) and were available in sufficient amounts, *i.e.* specimens from Montana and no. 100-793, L26368 and 21739 from Narsarsuk.

Bands in the 4000-3000 cm^{-1} range indicate the presence of O-H bonds in specimens from Montana and Narsarsuk, no. 100-793 and L26368, (Fig. 5). The general features of these spectra are essentially constant and do not reflect fluctuations of composition, as is the case in most OH-bearing minerals. Three high-intensity bands are observed at 3550 ± 2 , 3478 ± 2 and 3416 ± 2 cm^{-1} , and a low-intensity band at 3235 ± 1 cm^{-1} . All these bands are large and exhibit numerous shoulders. For example, the band width at half-height is about 70 cm^{-1} for the two external high-intensity bands and at least 85 cm^{-1} for the central band at 3478 cm^{-1} . The infrared spectrum performed on specimen 21739 (also from Narsarsuk), showing no band in the 4000-3000 cm^{-1} region, points to anhydrous composition, but is analogous to those of the 100-793 and L26368 specimens in the 1400-400 cm^{-1} region, where vibrations characteristic of the silicate structure are observed.

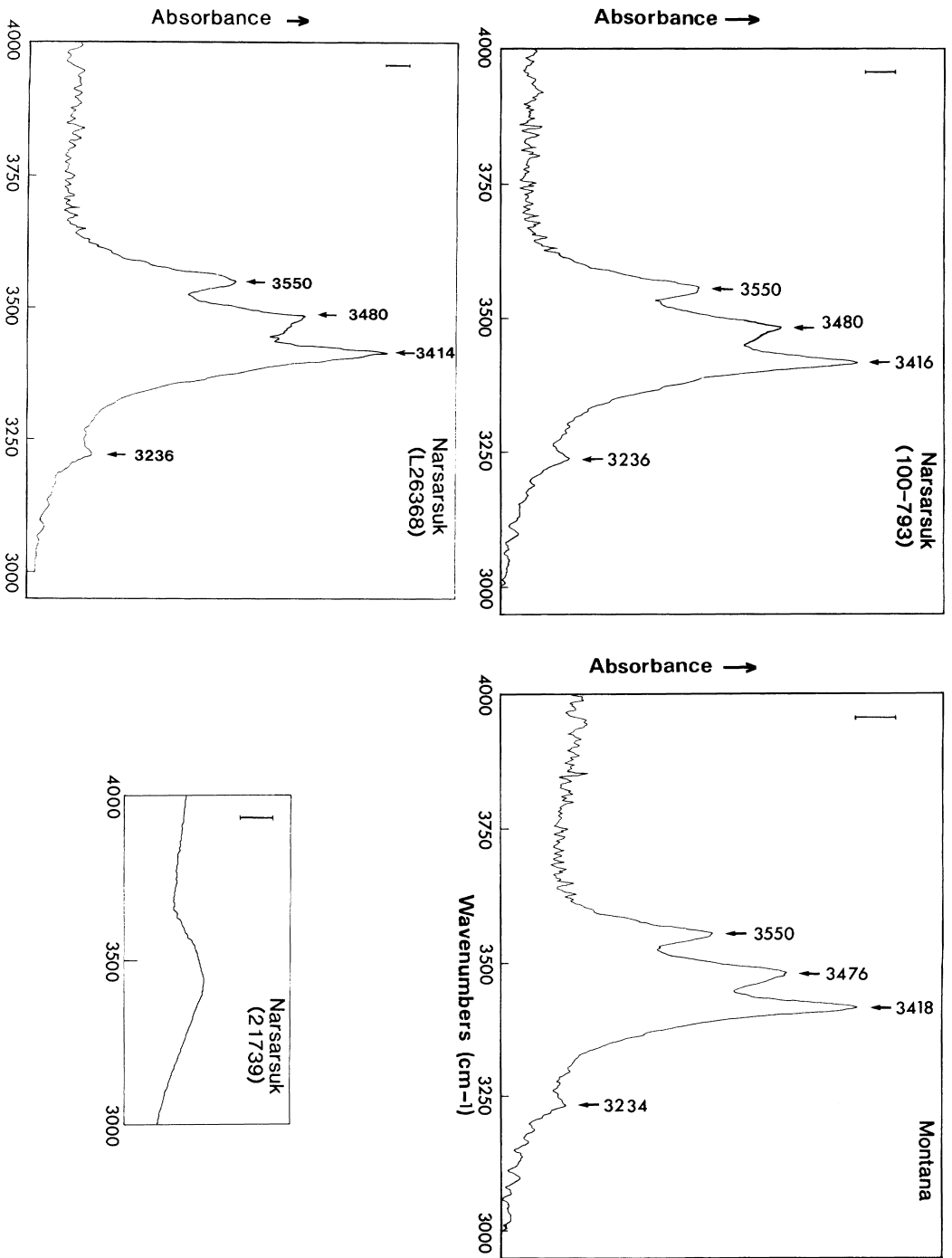


Fig. 5. Infrared absorption spectra (4000-3000 cm^{-1} range) of narsarsukites from Montana and Narsarsuk (specimens 100-793, L26368 and 21739). Scale bars correspond to 5 % absorbance.

Discussion

Bands in the 4000-3000 cm^{-1} range can be interpreted in two different ways: hydroxyls or water molecules. We examine below the two possibilities.

Underbonded oxygens of the theoretical H-free structure could trap protons and become hydroxyls. Local charge balance on anions was first discussed by Pyatenko & Pudovkina (1960) and Peacor & Buerger (1962), basing their conclusions on Pauling's electrostatic valence rule. We use part of their conclusions but we have recalculated the bond valences according to Brown & Altermatt (1985). The bond-valence exchange in a M-anion bond can be estimated by the relationship between bond-length (r) and bond-valence (s): $s = \exp[(r_0 - r)/B]$ where r_0 and B are empirical constants (Brown & Altermatt, 1985) and "r" values are those given by Peacor & Buerger (1962). According to these authors and Pyatenko & Pudovkina (1960), there are five independent oxygens: the apical oxygens of the titanium octahedra are O(1) and O(2), while O(3) and O(5) are shared between SiO_4 tetrahedra and O(4) are shared between octahedra and tetrahedra. Na is located in structure cavities bounded with seven oxygens. The valence sum of bonds reaching anion (Σ_{av}) is then calculated assuming the following M-anion bonds: O(1) is bonded to 2Ti, O(2) to 2Ti + 4Na, O(3) to 2Si, O(4) to Ti + Si + 2Na, O(5) to 2Si + Na. The results of valence sum calculations are reported in Table 5.

O(1) and O(2), which receive 1.572 and 1.644 valence units (v.u.) respectively, are strongly underbonded and thus are possible proton acceptors, particularly if we consider that Ti^{4+} may be partially replaced by Fe^{3+} ; additionally a positional disordering of Na is expected in that case. The weakness of the O-H bond strength within hypothetical hydroxyls (only 0.428 v.u. is exchanged within the O(1)H group for example) would explain the low OH-stretching wavenumbers, certainly below 3600 cm^{-1} (Robert & Kodama, 1988).

A comparison can be made with sphene, which shows similar single chains of corner-sharing Ti-octahedra with the possible introduction of F and OH (Mongiorgi & Riva di Sanseverino, 1968). Among the three different types of oxygens, only the O(1) oxygens, shared by two adjacent Ti-octahedra, are strongly under-

bonded (1.62 v.u.; Beran, 1970) and may be replaced by monovalent anions according to the coupled substitution $\text{M}^{3+} + (\text{OH}, \text{F}) = \text{Ti} + \text{O}(1)$ (Higgins & Ribbe, 1976). The corresponding OH-stretching wavenumber is 3448 cm^{-1} (Beran, 1970).

At the end of this discussion about the presence of hydroxyls in the narsarsukite structure, several major questions remain:

1 - May H^+ enter the narsarsukite structure, in the lack of a trivalent octahedrally coordinated cation? We have seen that even the theoretical narsarsukite end-member shows strong charge imbalance on oxygens O(1) and O(2).

2 - Why are there several bands, at least four, whereas only two oxygens can be protonated?

3 - Why are the bands so wide? 70-80 cm^{-1} are unusually high values for OH-stretching bands in hydroxyls.

4 - Why are there so little changes in the spectra (compare no. 100-793, L26368 and Montana, Fig. 5)? They do not reflect compositional variations, neither concerning band intensities, nor concerning wavenumbers, whereas it is well known that OH-stretching wavenumbers are extremely sensitive to perturbations of their close environment.

5 - How could the substitution operative in titanite ($\text{Fe}^{3+} + \text{OH} = \text{Ti}^{4+} + \text{O}$) play a significant role in narsarsukite, as the charge imbalance due to Fe^{3+} incorporation is entirely compensated by F^- alone (see Table 1 and Fig. 4)? Furthermore, the Fe^{3+} content is very fluctuating (0.113 atom p.f.u. in the Montana sample and 0.320 atom p.f.u. in sample 100-793 while the sum of oxides plus F remains approximately constant.

Table 5. Bond-lengths, r (\AA) and bond-valences, s (v.u.) for narsarsukite. "r" values from Peacor & Buerger (1962); Σ_{cv} : valence sum of bonds emanating from cation; Σ_{av} : valence sum bonds reaching anion.

	Ti		Si		Na		Σ_{av}
	r	s	r	s	r	s	
O(1)	1.904	0.786					1.572
O(2)	2.070	0.502					1.644
O(3)			1.626	0.995			1.990
O(4)	1.966	0.665	1.601	1.064	2.389	0.205	
	"	"			"	"	2.017
	"	"			2.723	0.083	
	"	"			"	"	
O(5)			1.639	0.960	2.522	0.143	2.130
			1.614	1.027	"	"	
Σ_{cv}	3.948		4.046		1.022		

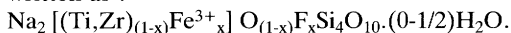
In order to answer these questions, we propose an alternative hypothesis. The bands observed in the 4000-3000 cm^{-1} range could be assigned to water molecules located in the large sodium cavities. These water molecules are bonded to the undersaturated oxygens O(1) and O(2) by hydrogen bonds $\text{OH}\cdots\text{O}(1,2)$. This situation is the same as that of zeolites, with which several spectral similarities are observed :

— The wavenumber range is the same : for example, main absorption bands at 3550 and 3405 cm^{-1} in natrolite ; series of bands observed between 3598 and 3235 cm^{-1} , with peaks at 3515 and 3415 cm^{-1} in scolecite ; similar bands are also known in heulandite, clinoptilolite, stilbite, phillipsite, gismondine, mordenite and chabazite (Kodama, 1985).

— The band widths are large (several tens cm^{-1}), like in narsarsukite.

— The band multiplicity can be explained by the multiplicity of water types and water-framework interactions and by the existence of the symmetric (ν_1) and antisymmetric (ν_3) internal vibrations of the water molecule. The situation of narsarsukite is also similar to that of epididymite, a triple-chain silicate, which contains one water molecule p.f.u. and whose spectrum shows two bands at 3552 cm^{-1} (ν_3) and 3470 cm^{-1} (ν_1) (Stavitskaya *et al.*, 1967).

We tentatively conclude that the presence of water molecules seems likely in narsarsukite. It accounts for the constancy of the IR spectra in the 4000-3000 cm^{-1} range as the cationic composition changes, and it is compatible with the Fe^{3+} - F correlation since it does not modify the bulk electrical neutrality, as OH would do. Considering the low analytical total, the amount of water is estimated about 2 %, which closely corresponds to the presence of 1/2 water molecule in the narsarsukite structure. The specimens from Mont St Hilaire, Quebec, and from Narsarsuk (no. 21739) seem to be H_2O -free. The general formula may be written as :



It can be noticed that the entry of F and that of water molecules do not follow the same scheme. The introduction of F (or very little OH) is always coupled with the replacement of Ti by Fe^{3+} and, to a lesser extent, by M^{2+} ; the presence of zeolitic water accounts for protons not involved in this mechanism. Of course, these water molecules are not necessa-

rily primary in narsarsukite and may have been trapped during later stages of rock evolution.

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