The Na$_{2-n}$H$_n$[Zr(Si$_2$O$_7$)]·mH$_2$O family of minerals and related compounds ($n = 0–0.5; m = 0.1$) consist of keldyshite, Na$_3$H[Zr$_2$(Si$_2$O$_7$)$_2$], and parakeldyshite, Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O. The crystal structures of these materials are based upon microporous heteropolyhedral frameworks formed by linkage of Si$_2$O$_7$ groups and ZrO$_6$ octahedra with internal channels occupied by Na$^+$ cations and H$_2$O molecules. The members of the family have been studied by the combination of theoretical (geometrical–topological analysis, Voronoi migration map calculation, and structural complexity calculation), and empirical methods (single-crystal X-ray diffraction, microprobe analysis, and Raman spectroscopy for parakeldyshite). It was found that keldyshite and parakeldyshite have the same fsh topology, while Na$_2$ZrSi$_2$O$_7$·H$_2$O is different and has the xat topology. The microporous heteropolyhedral frameworks in these materials have a 2-D system of channels suitable for the Na$^+$ ion migration. The crystal structure of keldyshite can be derived from that of parakeldyshite by the Na$^+$ + O$_2^-$ ↔ OH$^-$ + □ substitution mechanism, widespread in the postcrystallization processes in hyperagpaitic rocks.

Keywords: keldyshite; parakeldyshite; crystal structure; ion migration; transformation; Raman spectroscopy; Voronoi analysis; topology

1. Introduction

Microporous zirconosilicates attract considerable interest as ionic conductors, molecular sieves, and ion exchangers [1–3]. Among them, compounds with the NASICON-type structures are considered...
as ionic conductors, while sodium amphoterosilicates (e.g., ETS-4) are of interest as selective adsorbents for $^{137}$Cs and $^{90}$Sr radioactive isotopes [2,4–10]. The beginning of the study of zirconium silicate was stimulated by the discovery of keldyshite-group minerals in the Lovozero alkaline massif, Kola peninsula, Russia [11–15].

Keldyshite, (Na,H)$_2$[Zr(Si$_2$O$_7$)], was discovered in 1962 and the further detailed study of its holotype material indicated the existence in the mineral sample of polysynthetic intergrowths of two phases Na$_3$HZr$_2$(Si$_2$O$_7$)$_2$ and Na$_2$[Zr(Si$_2$O$_7$)] (renamed as keldyshite and parakeldyshite, respectively) [16]. The crystal-structure model for parakeldyshite was proposed in 1970 [17] and confirmed in 1974 [18]. The crystal structure of keldyshite was determined in 1978 [19], when the similarity between the crystal structures of keldyshite and parakeldyshite was demonstrated. The “M-34 phase” with the idealized chemical formula NaH[Zr$_2$(Si$_2$O$_7$)]·H$_2$O was discovered in the samples of parakeldyshite from Khibiny alkaline massif, but its crystal structure remains unknown [16].

General mineralogical and structural relationships between keldyshite, parakeldyshite, and the “M-34 phase” allowed establishment of the ‘parakeldyshite → keldyshite → “M-34 phase”’ transformational group of minerals (similar to the ‘kazakovite → tisinalite’ [20], ‘zirsinalite → lovozerite’ [21], etc. series). Within each group, transformation of the minerals is induced by ion-exchange reactions under natural conditions [22–26].

Synthetic zirconium silicates related to keldyshite are known [5,6] and can be obtained by different methods: (i) by crystallization from a melt at the temperature range 1000–1250 °C or (ii) by the hydrothermal technique at the temperatures of 450–500 °C [1,3]. Recently, an alternative model of the arrangement of Na cations in parakeldyshite was obtained [27] and the phase Na$_2$ZrSi$_2$O$_7$·H$_2$O was discovered, which is close in composition to the M-34 phase [28]. Keldyshite-related compounds have serious potential for their use in the purification of gases from sulfur dioxide in the production of sulfuric acid and heavy non-ferrous metals from sulfide ores [29]. Further work determined the presence of ion-exchange properties in the new zirconosilicate minerals discovered on the territory of the Kola alkaline province [27,30–32].

In this paper, we report the results of the theoretical analysis of the Na$^+$-ion migration paths in the crystal structures of keldyshite, parakeldyshite, and zirconium silicate Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O using a geometrical and topological approach [33,34]. The crystal structure of parakeldyshite was refined using the sample from albitized pegmatite at Takhtarvumchorr Mt., Khibiny alkaline massif, Russia. The transformational nature of keldyshite-related minerals is discussed.

2. Materials and Methods

2.1. Sample

A sample of parakeldyshite was collected from albitized pegmatites at the Takhtarvumchorr Mt. (Khibiny massif). Albite-rich is composed of a fine-fine-grained aggregate of lamellar albite with lenses (up to 1 × 0.5 m) of sugar-like apatite. The mass contains flattened prismatic crystals of enigmatite, flakes and radial-radial aggregates of molybdenite, plates of ilmenite and pyrrhotite, and dark-orange prismatic spherulites of pale cream fibrous chirvinskyte. Parakeldyshite was found as transparent barley-like crystals up to 2 mm long, with the marginal zones replaced by powdery precipitates of the “M-34 phase” [22] with the chemical composition NaH[Zr(Si$_2$O$_7$)] (Figure 1). In association with parakeldyshite, spherulites of chirvinskyte, lemon-yellow radial-radial aggregates, and individual prismatic crystals of titanite (partially replaced by lorenzenite, eudialyte, and zircon grains) have been observed.
2.2. Composition

The chemical composition of parakeldyshite was determined at the ‘Geomodel’ resource center of St. Petersburg State University using the scanning electron microscope Hitachi S-3400N equipped by INCA 500 WDS detector operating at 20–30 nA and 20 kV. The analyses were performed with the beam size of 5 μm and the counting time of 10–20/10 s on peaks/background for each chemical element. Quartz (Si), corundum (Al), calcite (Ca), halite (Na), zircon (Zr), rutile (Ti), hematite (Fe), celestine (Sr), and rhodonite (Mn) were used as standards. An average chemical composition based on 5 analyzes (in wt.%): ZrO$_2$ 39.95, Na$_2$O 20.02 SiO$_2$ 39.41, sum 99.38. The empirical formula calculated per 5 cations can be written as: Na$_{1.99}$Zr$_{0.99}$Si$_{2.02}$O$_{7.015}$.

2.3. Single-Crystal X-ray Diffraction

The crystal-structure studies of parakeldyshite were carried out at the X-ray Diffraction Resource Centre of St. Petersburg State University on an Agilent Technologies Xcalibur EOS diffractometer equipped with the CCD detector using monochromatic MoKα radiation (λ = 0.71069 Å) at room temperature. More than a hemisphere of diffraction data was collected (scanning step 1°, exposure time 10 s). The absorption correction was done empirically using spherical harmonics implemented in the SCALE ABSPACK calibration algorithm in the CrysAlisPro software package [35]. The unit-cell parameters were determined and refined by the least squares method using 1364 independent reflections. The data are deposited in CCDC under Entry No. 22040710. The coordination number of Na determined by number bonds with maximal length constrained 3.10 Å. Crystal data, data collection information, and refinement details are given in Table 1. Atom coordinates and isotropic parameters of atomic displacements are given in Table S1, interatomic distances in Table S2, and the anisotropic parameters of atomic displacements are given in Table S3.

![Figure 1. Powdered aggregates of parakeldyshite/keldyshite (1) in association with eudialyte (2), aegirine (3), albite (4), and låvenite (5) in albitized pegmatite in foyaites at Takhtarvumchorr Mt.](image-url)
Table 1. Crystal data, data collection information, and refinement details for parakeldyshite from Takhtarvumchorr Mt., Khibiny, Russia.

| Parameter                  | Data                      |
|----------------------------|---------------------------|
| Temperature/K              | 293(2)                    |
| Crystal system             | triclinic                 |
| Space group                | P1                        |
| a/Å                        | 5.4243(6)                 |
| b/ Å                       | 6.5923(5)                 |
| c/Å                        | 8.8083(6)                 |
| α/°                       | 71.309(7)                 |
| β/°                       | 87.162(8)                 |
| γ/°                       | 85.497(8)                 |
| Volume/Å³                  | 297.34(5)                 |
| Z                          | 2                         |
| ρcalc/g cm⁻³               | 3.411                     |
| µ/mm⁻¹                     | 2.388                     |
| F(000)                     | 292.0                     |
| Crystal size/mm³           | 0.17 × 0.12 × 0.11        |
| Radiation                  | Mo Kα (λ = 0.71073)       |
| 2θ range for data collection/° | 6.538 to 54.986     |
| Index ranges               | −5 ≤ h ≤ 7, −8 ≤ k ≤ 8, −11 ≤ l ≤ 10 |
| Reflections collected      | 2296                      |
| Independent reflections    | 1364 [Rint = 0.0221, Rσ = 0.0362] |
| Data/restraints/parameters | 1364/0/109                |
| Goodness-of-fit on F²      | 1.120                     |
| Final R indexes [I ≥ 2σ(I)]| R₁ = 0.0237, wR₂ = 0.0602 |
| Final R indexes [all data] | R₁ = 0.0256, wR₂ = 0.0616 |
| Largest diff. peak/hole/e Å⁻³ | 0.79/−0.69               |

2.4. Geometrical–Topological Analysis

Geometrical–topological analysis of the crystal structures of keldyshite-related compounds was carried out using algorithms implemented in the ToposPro software package (https://topospro.com) [33]. Maps of the migration of Na⁺-ions were constructed by the Voronoi method, which was shown to be efficient for various types of ionic conductors [34,37,38]. The radius of an elementary channel (Rchan) suitable for Na⁺-ion migration was chosen as 2.0 Å, similar to that reported previously [38,39].

Topological analysis of the crystal structures of keldyshite-related compounds also included the determination of the type basic grid, the construction of tiling, and the search for topologically similar inorganic compounds. The base grid is a graph whose vertices are the centers of gravity of the structural units, i.e., SiO₄ tetrahedra and ZrO₆ octahedra [40]. After contraction of doubly connected nodes (“bridging” oxygen atoms), a 4,6-coordinated grid was obtained (Figure 2).

The topological classification of the atomic nets in crystal structures was carried out in accordance with the following basic principle [41]: atomic nets with the same set of topological indices (coordination sequence, vertex symbols) belong to the same topological type [42]. In the case of the presence of stable polyhedral units in the crystal structure, the classification was carried out according to the basic grid [40]. Determination of the topological mesh type was performed using the ToposPro complex of the TopCryst web service (http://topcryst.com), which contains data on about 190,000 topological types of the nets.

The tiling theory, which is actively used to study and analyze the crystal structures of zeolites [43] and zeolite-related materials with heteropolyhedral frameworks [44–46], was introduced and developed by M. O’Keefe [47]. This approach allows study of the smallest cavities in inorganic frameworks that can be used to fill the entire crystal space [47]. Since the grids in the crystal structures of keldyshite and parakeldyshite have the same topology, the set of tilings in these structures is the same.
2.5. Raman Spectroscopy

The Raman spectrum (RS) was obtained using a Horiba Jobin-Yvon LabRam HR 800 spectrometer (Geomodel Resource Center, St. Petersburg State University) from the surface of a parakeldyshite crystal at room temperature and a wavelength of 514 nm in the range from 4000 to 80 cm⁻¹. The baseline correction was carried out using the algorithms implemented in the OriginPro 8.1 software package.

3. Results

3.1. Single-Crystal X-ray Diffraction

The crystal structures of microporous zirconium silicates are based upon frameworks consisting of ZrO₆ octahedra and SiO₄ tetrahedra linked via common O atoms. According to the structural classification proposed by Ilyushin and Blatov [40], the crystal structures of keldyshite, NaH[Zr(Si₂O₇)], parakeldyshite, Na₂[Zr(Si₂O₇)], and Na₂[Zr(Si₂O₇)]·H₂O contain polyhedral microensembles (PME) MT₆ of the A-1 type (Figure 3).

Figure 3. Polyhedral microensemble of MT₆-type forms the frameworks in the crystal structures of parakeldyshite, keldyshite, and the phase Na₂[Zr(Si₂O₇)]·H₂O.

In the terms proposed in [5], the crystal structure of parakeldyshite can be described as a framework consisting of the M₂T₄-type secondary building units (SBUs) with Na atoms in adjacent cavities (Figure 4a). Each ZrO₆ octahedron is linked to six SiO₄ tetrahedra, which in turn are linked to two Zr octahedra each.
According to our data, there are no additional Na sites described in [27]. In contrast to keldyshite, there are two independent positions of Na1 and Na2 with a coordination number (CN) of 7, respectively. The uneven distribution of Na in the crystal structure of parakeldyshite (Figure 5a).

In general, the structure model proposed in [17] was confirmed. The bond lengths in polyhedra vary significantly and are equal to 2.047–2.139(2), 1.601–1.672(2), 1.600–1.669(2), 2.443–2.913(3), and 2.384–2.913(3) Å for the ZrO6, Si1O4, Si2O4, Na1O8, and Na2O7 polyhedra, respectively. The degrees of distortion of polyhedra (based on bond lengths) calculated according to Baur [48] for the Si1O4, Si2O4, ZrO6, Na1O8, and Na2O7 polyhedra are equal to 0.01369, 0.01171, 0.01626, 0.04376, and 0.07001, respectively. According to our data, there are no additional Na sites described in [27]. In contrast to keldyshite, there are two independent positions of Na1 and Na2 with a coordination number (CN) of 8, respectively, in the crystal structure of parakeldyshite (Figure 5a).

The crystal structure of keldyshite (Figure 5b) differs from that of parakeldyshite and contains only one independent Na site with sevenfold coordination. The uneven distribution of Na in keldyshite results in the slight framework deformation manifested by the change of the Si–O–Si angle of 126.7(9)° compared to 127.7(8)° in parakeldyshite. At the same time, the shape of the channels changes significantly and are equal to 2.047–2.139(2), 1.601–1.672(2), 1.600–1.669(2), 2.443–2.913(3), and 2.384–2.913(3) Å for the ZrO6, Si1O4, Si2O4, Na1O8, and Na2O7 polyhedra, respectively. The increasing Si-O-Si angle corresponds to the increasing size of the structure channels (Figure 6c,f).

The crystal structure of keldyshite (Figure 5b) differs from that of parakeldyshite and contains only one independent Na site with sevenfold coordination. The uneven distribution of Na in keldyshite results in the slight framework deformation manifested by the change of the Si–O–Si angle of 126.7(9)° compared to 127.7(8)° in parakeldyshite. At the same time, the shape of the channels changes significantly and are equal to 2.047–2.139(2), 1.601–1.672(2), 1.600–1.669(2), 2.443–2.913(3), and 2.384–2.913(3) Å for the ZrO6, Si1O4, Si2O4, Na1O8, and Na2O7 polyhedra, respectively. The degrees of distortion of polyhedra (based on bond lengths) calculated according to Baur [48] for the Si1O4, Si2O4, ZrO6, Na1O8, and Na2O7 polyhedra are equal to 0.01369, 0.01171, 0.01626, 0.04376, and 0.07001, respectively. According to our data, there are no additional Na sites described in [27]. In contrast to keldyshite, there are two independent positions of Na1 and Na2 with a coordination number (CN) of 8, respectively, in the crystal structure of parakeldyshite (Figure 5a).

In the terms proposed in [5], the crystal structure of parakeldyshite can be described as a 4-block in the crystal structure of keldyshite; (c) 4-block in the crystal structure of parakeldyshite; (d) 4-block in the crystal structure of parakeldyshite; (e) 4-block in the crystal structure of parakeldyshite.

**Figure 5.** Projections of the crystal structures of (a) parakeldyshite; (b) keldyshite (c) Na2[Zr(Si2O7)]·H2O. The SiO4 tetrahedra are blue, the ZrO6 octahedra are green, the Na atoms are yellow, and the O atoms are red.

The crystal structure of keldyshite (Figure 5b) differs from that of parakeldyshite and contains only one independent Na site with sevenfold coordination. The uneven distribution of Na in keldyshite results in the slight framework deformation manifested by the change of the Si–O–Si angle of 126.7(9)° compared to 127.7(8)° in parakeldyshite. At the same time, the shape of the channels changes significantly and are equal to 2.047–2.139(2), 1.601–1.672(2), 1.600–1.669(2), 2.443–2.913(3), and 2.384–2.913(3) Å for the ZrO6, Si1O4, Si2O4, Na1O8, and Na2O7 polyhedra, respectively. The increasing Si-O-Si angle corresponds to the increasing size of the structure channels (Figure 6c,f).
whereas another one is within the Crystals 2020 in keldyshite. In the crystal structure of Na$_3$In the case of Na$_2$[Zr(Si$_2$O$_7$)]

3.2. Topological Analysis

The topological type of the base grid in the crystal structures of keldyshite and parakeldyshite is fsh, while that in Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O is xat (Figure 7). Table 2 shows data on related inorganic compounds of the fsh and xat topological types. Keldyshite and parakeldyshite consists of one type of the [4$^3$.6$^3$] tiles formed by three four-membered rings and three six-membered rings (Figure 8). In the case of Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O, there are two types of tiles: [6$^3$.6$^3$] t-kah and [4$^6$.6$^3$] t-af (Figure 8). Na atoms are located inside all [4$^3$.6$^3$] tiles in parakeldyshite and only half of these tiles are filled in keldyshite. In the crystal structure of Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O, one Na site is located in the t-kah tile, whereas another one is within the t-af tile.

Figure 6. Projections of the MT layers in the crystal structures of (a,d) parakeldyshite; (b,e) keldyshite; (c,f) Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O.

Figure 7. Tiling representation of the crystal structures of: (a) parakeldyshite/keldyshite (the fsh topology); (b) phase Na$_2$[Zr(Si$_2$O$_7$)]·H$_2$O (the xat topology). The [4$^3$.6$^3$] tiles are shown as light-blue, the t-af and t-kah tiles in (b) are yellow and violet, respectively.
The most intense spectral lines are similar to those for parakeldyshite from the Alluaiv Mt. Crystals 2020 range 90–300 cm$^{-1}$ symmetric deformation vibration modes in SiO$_2$ bonds in tetrahedra [62]. Bands of di can be associated with symmetric stretching vibrations of the Si-O-Si bridging oxygen in sorosilicate attributed to symmetric vibration modes of similar bonds [60–62]. The non-typical band at 718 cm$^{-1}$ to asymmetric stretching vibrations of Si-O-Si bonds, while three bands at 850, 905, and 941 cm$^{-1}$ stretching vibrations of Si-O bonds. Two intense absorption bands at 968 and 1017 cm$^{-1}$ to bending vibration modes of the Zr-O bonds in octahedra, and the bands in the range 90–300 cm$^{-1}$ correspond to symmetric bending vibrations of bonds in octahedra or translational

### Table 2. Examples of inorganic compounds with the grids of the fsh or xat topological type.

| Formula | Space Group | Topology | ICSD Code | Ref.   |
|---------|-------------|----------|-----------|--------|
| NaH[Zr(Si$_2$O$_7$)] | $\bar{P}\bar{I}$ | fsh | 20186 | [47] |
| keldyshite | | | | |
| Na$_2$[Zr(Si$_2$O$_7$)] | $\bar{P}\bar{I}$ | fsh | – | This work |
| parakeldyshite | | | | |
| K$_2$[Zr(Si$_2$O$_7$)] | $P2_1/b$ | fsh | 20100 | [49] |
| khibinskite | | | | |
| K$_2$[Zr(Ge$_2$O$_7$)] | C2/c | fsh | 88843 | [50] |
| K$_2$[Cd(P$_2$O$_7$)] | C2/c | fsh | 12117 | [51] |
| Na[Ti(P$_2$O$_7$)] | P2$_1$/c | fsh | 202751 | [52] |
| Na$_2$[Si$^{IV}$Si$_{IV}$O$_{10}$] | C2/c | fsh | 81134 | [53] |
| Na$_2$[Zr(Si$_2$O$_7$)]H$_2$O | C2/c | xat | 419420 | [28] |
| K[YP$_2$O$_7$] | Cmcm | xat | 75171 | [54] |
| Ba$_6$Dy$_2$Al$_4$O$_{15}$ | Cmcm | xat | 85071 | [55] |
| Si(P$_2$O$_7$) | P6$_3$ | xat | 75116 | [56] |
| Tm(BO$_3$) | P6$_3$2 | xat | 27942 | [57] |
| Na$_3$[Sc(Si$_2$O$_7$)] | P6$_3$mm | xat | 20120 | [58] |

![Figure 7. Tiling representation of the crystal structures and the corresponding tiles. The [43.63] tile is present in the crystal structures of keldyshite and parakeldyshite, while the t-kah and t-afo tiles are present in Na$_2$[Zr(Si$_2$O$_7$)]H$_2$O.](image)

#### 3.3. Raman Spectroscopy

The Raman spectrum of parakeldyshite from the albities of Takhtarvumchorr Mt. is shown in (Figure 9). The most intense spectral lines are similar to those for parakeldyshite from the Alluaiv Mt., Lovozero alkaline massif [52], RRUF, 120048 [59]. The bands in the range 850–1020 cm$^{-1}$ correspond to stretching vibrations of Si-O bonds. Two intense absorption bands at 968 and 1017 cm$^{-1}$ are attributed to asymmetric stretching vibrations of Si-O-Si bonds, while three bands at 850, 905, and 941 cm$^{-1}$ are attributed to symmetric vibration modes of similar bonds [60–62]. The non-typical band at 718 cm$^{-1}$ can be associated with symmetric stretching vibrations of the Si-O-Si bridging oxygen in sorosilicate groups [63]. The bands in the range 450–600 cm$^{-1}$ correspond to asymmetric bending vibrations of Si-O bonds in tetrahedra [62]. Bands of different intensities in the region 350–450 cm$^{-1}$ belong to symmetric deformation vibration modes in SiO$_4$ tetrahedra [63]. The most intense absorption band at 331 cm$^{-1}$ is attributed to bending vibration modes of the Zr-O bonds in octahedra, and the bands in the range 90–300 cm$^{-1}$ correspond to symmetric bending vibrations of bonds in octahedra or translational
vibrations \([64]\). The absence of bands in the region 3000–3800 cm\(^{-1}\) (Figure S1) indicates the absence of OH groups in the structure of parakeldyshite, confirming its unchanged nature.

![Figure 9. Raman spectrum of parakeldyshite from Takhtarvumchorr Mt., Khibiny, Russia.](image)

4. Discussion

According to the approach of matrix (self)assembly of the crystal structures from SBUs proposed by Ilyushin for sodium zirconium silicates, all possible SBUs variants are defined as \(M_2T_n\) \((n = 2, 4, 6)\) \([5]\). The crystal structure of keldyshite/parakeldyshite is based upon the \(M_2T_4\) blocks, while the structure of \(Na_2[Zr(SiO_7)]\cdot H_2O\) is based upon the \(M_2T_6\) blocks. This fact indicates different formation conditions and the impossibility of the transformation of one structure type into another through the rearrangement of \(Na^+\)-ions. Indeed, the conditions of the formation of phases in the \(Na_2CO_3-ZrO_2-SiO_2-H_2O\) hydrothermal system are different: parakeldyshite crystallizes at 450 °C \([5]\), while the \(Na_2[Zr(SiO_2)_2]H_2O\) phase appears at a temperature of about 200 °C \([28]\). According to \([65]\), keldyshite is a product of the sequential transformation of parakeldyshite under hypergenic conditions with the preservation of the overall framework topology. According to our data on the migration of \(Na^+\)-ions, such transition is possible.

The unit-cell parameters (Table 3) of keldyshite and parakeldyshite are close to each other and differ from those of \(Na_2[Zr(SiO_2)_2]\cdot H_2O\).

| Compound                  | Sp. Gr., Z | Unit Cell Parameters | \(V, \text{Å}^3\) | Citation               |
|---------------------------|------------|----------------------|------------------|------------------------|
| Keldyshite                | \(\beta\), 2 | \(a, 9.01\), \(b, 5.34\), \(c, 6.96\) | 300.39            | \([19]\)               |
| NaH\([Zr(SiO_2)_7]\)    | \(\beta\), 2 | \(a, 8.8083\), \(b, 5.4243\), \(c, 6.5923\) | 297.34            | Current work           |
| Parakeldyshite            | \(\beta\), 2 | \(a, 87.162\), \(b, 85.497\), \(c, 71.309\) | 672.2             | \([27]\)               |

Note. For parakeldyshite, the same setting as in the initial study of keldyshite was used (associated with that given in this work by the transition matrix 0 1 0 0 0 1/1 0 0).
The paths of the Na\(^+\)-ion migration obtained using the Voronoi method are two-dimensional, running through all the crystallographic positions of Na (Figure 10). Thus, the migration of Na\(^+\)-ions in the keldyshite-related zirconium silicates occurs along a two-periodic network of channels. Diffusion is possible when Na\(^+\)-ions move from cavity to cavity (from one tile to another) through four-membered and six-membered rings. Calculating the radius of these rings (Table 4) and comparing it with the threshold value of 2.0 Å, we can conclude that free migration of Na\(^+\) in these structures will occur only through six-membered rings. Moreover, in the case of parakeldyshite, there is one six-membered ring that is too narrow (marked in red in Table 4) for sodium to move along. However, the migration paths through the remaining six-membered rings form a 2-D migration map, which is consistent with the result obtained by the Voronoi method.

![Figure 10. Migration paths of Na\(^+\) cations obtained using the Voronoi method for the structures: (a) parakeldyshite; (b) keldyshite.](image)

**Table 4.** The radii of the rings for the possible migration of Na\(^+\) cations in the structures of keldyshite, parakeldyshite, and Na\(_2\)ZrSi\(_2\)O\(_7\)-H\(_2\)O calculated using the geometric-topological approach.

| Compound               | Number of Nodes in the Ring | Radius of Ring, Å | Compound               | Number of Nodes in the Ring | Radius of Ring, Å |
|------------------------|-----------------------------|-------------------|------------------------|-----------------------------|-------------------|
| Parakeldyshite         | 6                           | 2.12              | Na\(_2\)ZrSi\(_2\)O\(_7\)-H\(_2\)O | 6                           | 1.77              |
| Na\(_2\)ZrSi\(_2\)O\(_7\) | 6                           | 2.06              | Keldyshite             | 6                           | 2.00              |
|                        | 6                           | 1.75              | NaZr(Si\(_2\)O\(_3\))OH | 4                           | 1.84              |
|                        | 6                           | 2.14              |                        | 4                           | 1.37              |
|                        | 4                           | 2.06              |                        | 4                           | 1.77              |
|                        | 6                           | 1.75              |                        | 4                           | 1.78              |

The refinement of the crystal structure of parakeldyshite from the Takhtarvumchorr pegmatite demonstrates the absence of splitting of the Na sites. According to the chemical data and Raman spectroscopy, the studied sample of parakeldyshite is the extreme Na-member of the possible keldyshite-parakeldyshite series. The migration paths analysis by the Voronoi method showed that all three studied phases have a 2-D system of channels (Figures 10 and 11), within which the migration of Na\(^+\) cations is possible. These data confirm the possibility of transition from
parakeldyshite to keldyshite by the Na⁺ + O₂⁻ ↔ OH⁻ + □ substitution scheme, which is widespread in postcrystallization processes in peralkaline rocks.

Figure 11. Migration paths of Na⁺ cations obtained using the Voronoi method for the crystal structure of Na₂[Zr(Si₂O₇)]·H₂O.

The structural complexity I_G, total was calculated according to the method proposed in [66]. The calculated values for keldyshite/parakeldyshite and Na₂ZrSi₂O₇·H₂O are 76.107 and 86.606 (bits/u.c.), respectively. The identity of the structural complexity values for keldyshite and parakeldyshite emphasizes their structural similarity. The increase in structural complexity with the decreasing crystallization temperature is in agreement with the general tendency observed for hydrothermal systems [66,67].

Supplementary Materials: The following materials are available online at http://www.mdpi.com/2073-4352/10/11/1016/s1, Figure S1: title, Table S1: Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³) for parakeldyshite. Table S2: selected interatomic distances in parakeldyshite. Table S3: anisotropic parameters of atomic displacements in parakeldyshite.

Author Contributions: N.A.K. and T.L.P. designed the study. V.V.S. and N.S.V. performed microprobe analyses, V.N.Y. provide samples for investigation. V.N.B. performed Raman spectroscopy measurements, T.L.P. performed and interpreted Single-crystal X-ray diffraction experiments. N.A.K., T.L.P. and S.M.A. wrote the draft paper. S.V.K. supervising, review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Kola Science Center of Russian Academy of Sciences (Project 0226-2019-0011) and funded by the Russian Foundation for Basic Research (Grant 18-29-12039). N.A.K. thanks the Ministry of Education and Science of the Russian Federation for financial support within grant No. 0778-2020-0005.

Acknowledgments: Technical support by the SPbSU X-ray Diffraction and ‘Geomodel’ Resource Centers is gratefully acknowledged. There are two anonymous reviewers are thanked for fruitful remarks and corrections.

Conflicts of Interest: The authors declare no conflict of interest.

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