

Si, Al, Fe order-disorder in Fe-bearing K-feldspar from Madagascar and its implications to Ar diffusion

Autor(en): **Nyfeler, Daniel / Armbruster, Thomas / Villa, Igor M.**

Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **78 (1998)**

Heft 1

PDF erstellt am: **18.09.2024**

Persistenter Link: <https://doi.org/10.5169/seals-59271>

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern.

Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.

Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

Si, Al, Fe order-disorder in Fe-bearing K-feldspar from Madagascar and its implications to Ar diffusion

by Daniel Nyfeler¹, Thomas Armbruster¹ and Igor M. Villa²

Abstract

The crystal structure of monoclinic K-feldspar from Itrongay, Madagascar, $(K_{0.95}Na_{0.05})[Al_{0.95}Fe_{0.05}^{3+}Si_3O_8]$ was studied with single-crystal X-ray diffraction data in its natural state and after tempering various times (3 h up to 672 h) between 750 and 950 °C. Natural Itrongay K-feldspar possesses a Si,Al distribution characteristic of low-sanidine ($t_i = 0.352$) with Fe enriched on the T₁ site (space group $C2/m$, $a = 8.5820(6)$, $b = 13.003(2)$, $c = 7.1924(7)$ Å, $\beta = 116.02(1)$ °). Heating at 750 °C (672 h) and short time heating (< 18 h) at 950 °C has no measurable effect on Si,Al ordering. After 672 h at 900 °C Si,Al becomes more disordered ($t_i = 0.273$), though variable from crystal to crystal, reaching the Si,Al distribution of high-sanidine (space group $C2/m$, $a = 8.568(2)$, $b = 13.030(2)$, $c = 7.1745(9)$ Å, $\beta = 115.99(1)$ °). With increasing Si,Al disorder Fe becomes more equally distributed between T₁ and T₂. Natural single crystals of Itrongay K-feldspar are rather ideal with no pronounced mosaic pattern as determined by a high empirical X-ray extinction coefficient. This coefficient varies from crystal to crystal but prolonged heating above 900 °C seems to reduce this value indicating formation of mosaic blocks with heating. Si,Al interdiffusion was faster than Ar diffusion in our aliquot. It is suggested that Ar diffusion upon heating is linked to T-O breaking and thus mainly a consequence of Si,Al rearrangement.

Keywords: K-feldspar, order-disorder. Ar diffusion, X-ray diffraction.

Introduction

A long-standing problem in geochronology is the interpretation of mineral ages derived from K-feldspar. An acute controversy regards the legitimation of using its Ar release to determine its diffusivity. In this approach (ARNAUD and KELLEY, 1997, and references therein), the release of ³⁹Ar in K-feldspar is used both to determine an age and to calculate a Fickian diffusion coefficient during the same experiment. However, an alternate view (VILLA, 1994) holds that the release of Ar from K-feldspar is not a Fickian process, so that translating a dating experiment into a cooling rate is, as a rule, not legitimate. To do that, it would be necessary first to assess the mechanisms by which Ar diffuses through the lattice, and to demonstrate that only one single Fickian process is operating. Ar diffusion was investigated on chips of a gem-

quality single crystal of Itrongay K-feldspar (VILLA, 1996). These experiments showed strong deviations from classical diffusion models, i.e. showed clear evidence of a plurality of diffusion phenomena. The present study was undertaken to examine whether in the experimental conditions of the Ar runs the crystallographic characteristics of the chips were modified, and in particular to investigate the influence of Si,Al interdiffusion as a function of temperature and time.

Previous studies on feldspar from Madagascar

The first description of feldspars from Itrongay, Madagascar goes back to the beginning of this century when LACROIX (1912) reported yellow orthoclase of gem quality from a miarolitic pegmatite near Itrongay. SETO (1923) analyzed 2.93 wt%

¹ Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. <armbruster@krist.unibe.ch>

² Mineralogisch-petrographisches Institut, Isotopengeologie, Universität Bern, Erlachstrasse 9a, CH-3012 Bern, Switzerland.

Fe₂O₃, and showed a relation between depth of color, iron content and refractive indices. However, it must be mentioned that there are other pegmatitic occurrences in Madagascar where no significant Fe substitution was found for orthoclase (e.g., HARRIS et al., 1989). KÔZU and SUZUKI (1925), BARTH (1951) and SPENCER (1930; 1937) studied the influence of tempering on the optical properties of K-feldspars from various localities. SPENCER (1937) heated different samples progressively to 1120 °C and stated that K-feldspar from Madagascar shows a greater resistance to change of optic-axial angles than other K-feldspars. COOMBS (1954) reported the existence of highly irregular variations in 2V angle within one crystal and gave as explanation the influence of locally varying Fe³⁺ concentrations on the degree of Si,Al ordering. Based on the nowadays established assumption that Fe³⁺ preferentially replaces the smaller Al³⁺ (e.g., FAYE, 1969; HOFMEISTER and ROSSMAN, 1984) he considered a Fe³⁺ distribution corresponding to partial Al disorder as known for orthoclase and low-sanidine. WALTHER (1966) reported that the individual axes increase with Fe-concentration in the sequence $a > b > c$. PRIESS (1981) noticed manifold types of microscopic and macroscopic inclusions in Itrongay K-feldspar such as quartz, pyroxenes, various ore phases and fluid inclusions. Optical inhomogeneities became more apparent with heating but could not be related to chemical variations (PRIESS, 1981). GERING (1985) refined the crystal structure of Madagascar K-feldspar from single-crystal X-ray diffraction data. The Si,Al ordering pattern was characteristic of orthoclase but GERING (1985) neglected the possible effect of iron and did not state an analysis.

Si,Al ordering and symmetry in K-feldspars

Depending on the degree of Si,Al order K-feldspar is either monoclinic or triclinic. Two symmetry independent tetrahedral positions, T₁ and T₂ exist in the low ordered monoclinic modification, space group C2/m. The 4 Al and 12 Si atoms occupy 8 T₁ and 8 T₂ positions, thus, complete ordering is disabled. However, when the symmetry is lowered to triclinic, space group C1, the positions T₁ and T₂ split to T_{1o} and T_{1m}, and to T_{2o} and T_{2m}, respectively, enabling complete ordering (with Al on T_{1o}). Following KROLL and RIBBE (1983) t_i reflects the probability to occupy a tetrahedral site T_i with Al, thus $t_i = \text{Al}_i / (\text{Al}_i + \text{Si}_i)$. The following assumptions can be made (RIBBE, 1974):

monoclinic alkali feldspars $t_1 \geq t_2$,
 triclinic alkali feldspars $t_{1o} \geq t_{1m} \geq t_{2o} = t_{2m}$.

K-feldspars are considered to have triclinic symmetry when crystallized at low temperatures, and have monoclinic symmetry at higher crystallization temperatures. The nomenclature used in this study is based on RIBBE (1983) who defines the following structural limits for the terms high- and low-sanidine and orthoclase:

high-sanidine: $0.25 < t_1 < 0.333$

low-sanidine: $0.334 < t_1 < 0.37$

orthoclase: $0.37 < t_1 < 0.5$.

Triclinic potassium feldspars with complete and intermediate Si,Al ordering are called maximum microcline and intermediate microcline, respectively (BAILEY, 1969).

There are several direct and indirect methods to determine the degree of Si,Al order in alkali-feldspars, most of them rely on X-ray and neutron diffraction data. Using neutron diffractometry, structure refinements based on the different scattering powers of Al and Si provide accurate site occupancy factors. An alternative method is the application of empirically derived formulas using selected cell constants (KROLL and RIBBE, 1983). The unit cell volume and the monoclinic angle β turned out to be almost unaffected by varying Si,Al distribution. The b and c lengths depend on both the chemical composition and Si,Al order and are therefore sensitive to site occupancies in chemically invariant systems. The monoclinic nature of the K-feldspar from Itrongay restricts average site-occupancy determination to T₁ and T₂. The effect of Fe³⁺ ions on the tetrahedral sites, however, requires a specific treatment in the structure refinement procedure, as will be discussed in the experimental section.

Very sensitive methods to analyze Si,Al ordering in K-feldspars are *Hard Mode Infrared Spectroscopy* (HARRIS et al., 1989) and combined ²⁷Al-²⁹Si MAS NMR spectroscopy (XIAO et al., 1995). The latter technique, however, can only be applied to Fe-free samples. It is well established that K-feldspars with Si,Al ordering patterns according to low-sanidine or orthoclase (but not high-sanidine) exhibit a modulated or tweed structure when studied with the TEM (e.g., HARRIS et al., 1989; MCLAREN and FITZ GERALD, 1987; XIAO et al., 1995). It is generally agreed that the K-feldspar structures with the tweed pattern are similar to microcline, although with reduced Si,Al order, where the spontaneous strain is compensated by structural modulations (HARRIS et al., 1989).

To determine differences in the chemical compositions or Si,Al ordering in feldspars, optical methods are a sensitive and fast tool (GERING, 1985). A variety of such methods is proposed by TUTTLE (1952), COLVILLE and RIBBE (1968),

Stewart and RIBBE (1983), and SU et al. (1984). The transition from an ordered to a disordered Si,Al distribution in K-feldspar is accompanied by changes of the optical parameters (e.g., HEWLETT, 1959; KROLL and KNITTER, 1991) such as the optic-axial angle. However, the direct link between an observed optical feature and a structural property is far from being trivial (STEWART and RIBBE, 1983; GERING, 1985). In addition, the K-feldspars from Itrongay are known to have heterogeneous optical properties (GERING, 1985; WALTHER, 1966; COOMBS, 1954; SPENCER, 1937; PRIESS, 1981).

Fe³⁺ in K-feldspars

In natural feldspars, Fe³⁺ appears generally as a minor element < 5 weight % (SMITH, 1974). The Itrongay K-feldspar with a Fe concentration up to K[Al_{0.89}Fe_{0.11}Si₃O₈] (SETO, 1923; this study) is to our knowledge one of the Fe-richest natural K-feldspars reported. Yellow sanidine from Leucite Hills, Wyoming, contains even up to 18% of the KFeSi₃O₈ molecule (CARMICHAEL, 1967). A synthetic low-sanidine with the composition K[Al_{0.72}Fe_{0.28}Si₃O₈] was grown by NADEZHINA et al. (1993) under hydrothermal conditions at 525 °C (2 kbar). A subsequent single-crystal X-ray structure refinement yielded site occupancies for T₁ (Al_{0.24}Fe_{0.10}Si_{0.66}), and for T₂ (Al_{0.12}Fe_{0.04}Si_{0.84}). WONES and APPLEMAN (1961; 1963) synthesized K[FeSi₃O₈] hydrothermally between 1 and 2 kbars, with Si, Fe ordering characteristic of "iron-sanidine" at temperatures above 700 °C and with Si, Fe ordering characteristic of "iron-microcline" below 690 °C. A reversible phase transition between triclinic and monoclinic K[FeSi₃O₈] occurs at 704(6) °C and 2 kbar (WONES and APPLEMAN, 1963). The location and diffusion rate of trace Fe³⁺ in natural feldspars was investigated by PETROV et al. (1989) and PETROV and HAFNER (1988). They conclude that re-distribution of Fe³⁺ is subject of higher kinetic barriers than Si,Al re-distribution.

Experimental

The investigated sample is a large (several cm), yellowish K-feldspar crystal of gem quality from Itrongay, Madagascar. The crystal chip selected for analysis had a surface of 2–5 mm² and was transparent and homogeneous when inspected with the optical microscope. The chemical composition of the untreated sample was obtained using a SX-50 electron microprobe with standard operating conditions of 15 kV accelerating voltage and 15 nA sample current. The relative error for

major elements, determined for the standards, is < 1%. Natural orthoclase, albite and anorthite and synthetic almandine were used as standards for K, Ca, Na, Si, Al, and Fe. A net of 130 points, separated by ca. 100 μm each, was analyzed. The resulting formula was normalized to 5 cations and 8 oxygen atoms.

Heating experiments of all samples were carried out as described by VILLA (1994). Fragments of the single crystal analyzed by electron microprobe were heated at different temperatures and different times to investigate a possible increase of Si,Al disorder. Three different heating times (3 h, 12 h, 18 h) were chosen at 950 °C, and one long-time (28 days) experiment was performed at 900 °C. For each specific heating experiment, two crystals were investigated. Sample 5 represents another 950 °C experiment which was annealed for 12 hours in a different furnace. Additional experiments were performed at 750 °C for 14 days and 28 days (samples 2 a, b; Tab. 1).

In order to obtain precise unit-cell dimensions, 25 selected X-ray reflections with high- Θ angles (18–28 ° Θ) were centered on a conventional CAD4 single crystal X-ray diffractometer using Mo K α radiation. X-ray intensity data were collected on a SMART Siemens X-ray diffractometer equipped with a CCD detector, using Mo K α radiation and standard operating conditions (50 kV, 40 mA). The structure was refined with the program SHELX-93 (SHELDRICK, 1993), using scattering factors for neutral elements and allowing for anisotropic displacement parameters for all atoms. An extinction parameter x was refined by an empirically derived least-square term $k [1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin 2\Theta]^{-1/4}$ (SHELDRICK, 1993), where k is the overall scale factor. This X-ray extinction parameter allows for an estimation of the crystal perfection (BECKER and COPPENS, 1974; GERING, 1985) and represents a compromise to cover both primary and secondary extinction (SHELDRICK, 1993).

The contribution of 5% Na substituting for K as determined by electron microprobe (EMP) is considered in the structure refinement. The direct refinement of Si, Al, and Fe occupancies on the tetrahedral sites is inhibited by two reasons. For neutral atoms, the scattering power of Al with 13 electrons and Si with 14 electrons is very similar, and routine X-ray diffraction data using Mo radiation do not provide reliable accuracy for the distinction between Al and Si. In addition, the slight effect of Al to lower the observed electron density is balanced by the presence of ca 5% Fe (26 electrons) replacing Al. Thus, site occupancy factors cannot directly be refined. As a first approximation, the Si,Al site occupancy factors were de-

terminated based on cell dimensions following the empirically derived formula (KROLL and RIBBE, 1983)

$$2t_i = -7.590 - 2.3258 \cdot b + 5.3581 \cdot c$$

for monoclinic K-feldspars. For comparison, we have chosen a method based on the tetrahedral T-O bond lengths for an estimate of t_i , as proposed by KROLL and RIBBE (1983),

$$t_i = 0.25 + [(\langle T_i-O \rangle - \langle\langle T-O \rangle\rangle) / 0.125]$$

where $\langle T_i-O \rangle$ is the average cation-oxygen bond length of the observed tetrahedra, and $\langle\langle T-O \rangle\rangle$ is the grand mean average, the average of all the $\langle T_i-O \rangle$ in the unit cell (KROLL and RIBBE, 1983). The site occupancies for Al (derived from t_i) and Si (derived from $1-t_i$) were multiplied with their respective electron number to obtain a calculated electron density. This value is compared with an observed electron density refined for the individual T_i sites. The observed value was established by refining the site occupancy of T_i with a dummy Si placed at the respective site. The refined site occupancy multiplied by 14 reflects the observed electron density. The difference (obs-calc) allows for an assignment of the Fe contribution. The two differences for T_1 and T_2 were compared, and the larger value was considered to be indicative of Fe preference on the corresponding T site. The unbiased reader may wonder why the method was not exploited to determine a more exact distribution of Fe between T_1 and T_2 . However, the low average Fe^{3+} concentration in Itrongay K-feldspar, $(K_{0.95}Na_{0.05})[Al_{0.95}Fe_{0.05}^{3+}Si_3O_8]$, associated with the high standard deviations in this type of calculation did not allow further interpretations.

Results

The chemical composition of the Itrongay K-feldspar yielded an average composition of $(K_{0.94}Na_{0.051})[Al_{0.95}Fe_{0.05}Si_3O_8]$ with variations of $Na_{0.08}$ to $Na_{0.04}$ (98% of the analyses have $0.04 < Na < 0.06$) and of $Fe_{0.05}$ to $Fe_{0.01}$ (98% of the analyses have $0.04 < Fe < 0.05$). One Na rich outlier and two Fe poor outliers correspond to decreased content of K and increased content of Al, respectively. The cell dimensions of all samples are compiled in table 1. The parameters of the CCD data collection are listed in table 2, and the important figures of the structure refinement procedure are given in table 3.

³ Numbers in parentheses denote 1 σ uncertainty on the last digit.

Natural Itrongay K-feldspar is characterized by cell parameters of $a = 8.5820(6)^3$, $b = 13.003(2)$, $c = 7.1924(7)$ Å, $\beta = 116.022(7)^\circ$, and $V = 721.3(1)$ Å³. The Si,Al distribution (compiled in Tab. 4) of this sample is characteristic of low-sanidine ($t_i = 0.352(6)$) with Fe enriched on the T_1 site. Heating at 750 °C (672 h) and short-time heating (< 18 h) at 950 °C has no measurable effect on cell dimensions and Si,Al ordering. Based on the values of electron-density differences between T_1 and T_2 , Fe in samples 1.a to 6.a is assigned to T_1 . Sample 6.b (18 h, 950 °C) is characterized by $a = 8.581(1)$, $b = 13.006(1)$, $c = 7.187(1)$ Å, $\beta = 115.99(1)^\circ$, and $V = 721.0(2)$ Å³, and $t_i = 0.334(6)$. The latter t_i value is statistically different, at the 97% level, from the value of the untreated sample. After 672 h at 900 °C Si,Al becomes more disordered, though variable from crystal to crystal, reaching the Si,Al distribution of high-sanidine ($a = 8.568(2)$ Å, $b = 13.030(2)$ Å, $c = 7.1745(9)$ Å, $\beta = 115.99(1)^\circ$, $V = 720.0(2)$ Å³, and $t_i = 0.273(7)$). In samples 6.b to 7.b Fe is assumed to be equally distributed among T_1 and T_2 .

The atomic coordinates and both the isotropic and anisotropic displacement parameters of sample 1.a and 7.b are listed in table 5. The choice of scattering factors in these final refinements was adjusted to the estimated Fe, Al, Si distribution on the two tetrahedral sites.

Discussion

The average chemical composition measured in this study is in fair agreement with the previous investigations on Itrongay K-feldspar. COOMB'S (1954) wet chemical analysis yielded the formula $(K_{0.95}Na_{0.01})[Al_{0.94}Fe_{0.05}Si_3O_8]$, for another sample from the same locality he reported a K content of only 0.90, and tetrahedral Fe of 0.09. SETO (1923) states the composition $(K_{0.99}Na_{0.01})[Al_{0.95}Fe_{0.05}Si_3O_8]$.

Cell dimensions established in this study indicate that b slightly increases and c decreases in consequence to long-time (> 12 h) heating at high temperatures (> 900 °C). This behavior is in agreement with observations by KROLL and RIBBE (1983). The two methods to determine t_i , based on the unit cell dimensions b and c , and on $\langle T-O \rangle$, respectively, agree within 1 σ . The natural Itrongay K-feldspar possesses a Si,Al distribution characteristic of low-sanidine. Using Guinier-powder X-ray diffraction data GERING (1985) reported cell constants for Itrongay K-feldspar of $a = 8.578(1)$ Å, $b = 12.978(2)$ Å, $c = 7.204(1)$ Å, $\beta = 116.02(2)^\circ$. Based on the empirical formula of KROLL and RIBBE (1983) the cell dimensions of GERING'S

Tab. 1 Cell dimensions of differently heated Itrongay K-feldspars.

#	time [h]	T [°C]	a [Å]	b [Å]	c [Å]	β [°]	V [Å ³]
1. a	0	0	8.5820(6)	13.003(2)	7.1924(7)	116.022(7)	721.3(1)
b	0	0	8.5832(6)	13.002(2)	7.1925(5)	116.022(6)	721.3(1)
2. a	336	750	8.5830(9)	13.001(3)	7.192(2)	116.03(1)	721.1(2)
b	672	750	8.5831(9)	13.000(3)	7.1925(9)	116.030(9)	721.2(2)
3. a	3	950	8.582(1)	13.001(2)	7.1913(6)	116.018(8)	721.1(2)
b	3	950	8.584(1)	13.0020(9)	7.1920(6)	116.031(8)	721.2(1)
4. a	12	950	8.584(2)	13.002(1)	7.1915(6)	116.02(1)	721.3(2)
b	12	950	8.583(1)	13.004(1)	7.1920(6)	116.026(8)	721.3(1)
5	12	950	8.5837(8)	13.003(1)	7.1920(5)	116.010(7)	721.4(1)
6. a	18	950	8.5839(6)	13.006(3)	7.1901(8)	116.016(7)	721.4(2)
b	18	950	8.581(1)	13.006(1)	7.187(1)	115.99(1)	721.0(2)
7. a	672	900	8.579(1)	13.013(1)	7.1838(8)	116.00(1)	720.8(2)
b	672	900	8.568(2)	13.030(2)	7.1745(9)	115.99(1)	720.0(2)

(1985) investigation lead to $t_f = 0.412$, in comparison with $t_f = 0.424$ based on the <T-O> method. Thus, he interpreted Itrongay K-feldspar to be orthoclase, in contrast to the present study, where the ordering pattern agrees with low-sanidine.

The compilation in table 4 shows that temperatures ≤ 750 °C and short-time (≤ 12 h) heating at 950 °C do apparently not affect the average Si,Al distribution for T₁ and T₂ in Itrongay K-feldspar within the detection limits of the technique. SPENCER (1937) did not observe a change in the optical properties of K-feldspar from Madagascar upon short-time (< 2 h) heating to 1050 °C. GERING (1985) heated gem-quality sanidine from Eifel, Germany to 750 °C for 1'900 hours and observed $t_f = 0.293(4)$ in comparison to $t_f = 0.329(8)$ for the natural Eifel sanidine. Heating at 650 °C did not influence the Si,Al distribution. In a kinetic study of Si,Al ordering in Eifel sanidine KROLL and KNITTER (1991) report that a steady state at 650 °C would be reached only after several years, whereas steady state was reached after ca 2400 h at 750 °C and after ca. 240 h at 850 °C. The activation energy for Si,Al exchange was determined to be 223.0 (± 11.3) kJ/mol (KROLL and KNITTER, 1991). The long-time (672 h) experiments at 900 °C of the present study show an increased disorder in the tetrahedral sites (up to $t_f = 0.273(7)$), though varying from crystal to crystal. GERING'S (1985) experiments on Eifel sanidines yielded $t_f = 0.274$ when heated to 950 °C for 20 hours. As a consequence of its high Fe content, K-feldspar from Itrongay seems to display more sluggish reaction of the Si,Al re-distribution upon heating than Fe free K-feldspars (e.g., SPENCER, 1937; this study).

Our assignment of Fe to both T sites for the samples 6.b, 7.a, and 7.b indicates a diffusional behavior of Fe comparable to Al. An electron-para-

Tab. 2 CCD data collection of Itrongay K-feldspars.

Diffractometer	Siemens SMART CCD system
X-ray radiation	sealed tube MoK α
X-ray power	50 kV, 40 mA
Temperature	293 K
Detector to sample distance	5.18 cm
Detector 2 θ angle	27°
Resolution	0.77 Å
Rotation axis	ω
Rotation width	0.3°
Total number of frames	1271
Frame size	512 \times 512 pixels
Data collection time per frame	10 seconds
Collection mode	automated hemisphere

magnetic resonance (EPR) study (PETROV et al., 1989) on triclinic albite yielded Fe³⁺ site occupancy factors for T₁o remaining constant at 850 °C, whereas Si,Al disorder increased. PETROV and HAFNER (1988) considered sanidine to have trace Fe³⁺ disordered over T₁ and T₂, only slightly preferring T₁. They describe the kinetics for Fe³⁺ \leftrightarrow Al³⁺ as well as Fe³⁺ \leftrightarrow Si⁴⁺ exchange to be slow, probably slower than Al³⁺ \leftrightarrow Si⁴⁺ exchange. PETROV and HAFNER (1988) suggested that the nearly disordered distribution of Fe³⁺ in natural sanidine is interpreted as the consequence of a high kinetic barrier of the Fe \leftrightarrow Al exchange among T₁ and T₂ in the subsolidus range in alkali feldspars.

The empirical extinction parameters of the samples investigated in this study trend towards lower extinction with increased heating time and temperature (Tab. 3). The crystal perfection as es-

Tab. 3 Selected results of CCD data collection and structure refinement.

	1.a	1.b	2.a	2.b	3.a	3.b	4.a	4.b	5	6.a	6.b	7.a	7.b
Reflections measured	1962	1965	1947	1940	1939	2039	1954	1843	1965	1959	1947	1976	1934
max 2 θ angle	54.76	55.09	55.29	54.53	54.25	55.77	54.9	53.08	54.22	54.96	54.7	54.9	54.78
Unique reflections	784	797	781	779	784	831	779	729	785	791	796	781	789
Reflections > 2 σ (I)	754	773	643	718	771	788	710	675	714	753	770	748	771
R(int)	2.83	3.21	4.24	3.43	3.94	2.47	2.55	2.93	3.15	2.27	2.77	3.59	3.32
R(σ)	2.33	2.72	4.03	2.93	3.11	2.32	2.64	2.87	2.97	2.16	2.41	2.72	2.59
Number of least squares parameters	64	64	64	64	64	64	64	64	64	64	64	64	64
GooF	1.167	1.075	1.122	1.074	1.062	1.117	1.058	1.118	1.121	1.049	1.226	1.079	1.098
R1, $F_o > 4\sigma(F_o)$	2.28	2.18	3.46	2.57	2.25	2.15	2.56	2.54	2.41	2.17	2.24	2.43	2.47
R1, all data	2.4	2.26	4.89	2.89	2.29	2.32	2.96	2.78	2.77	2.31	2.34	2.54	2.53
wR2 (on F2)	6.79	6.58	9.27	7.22	6.68	6.08	7.08	7.33	6.82	6.6	7.58	6.96	7.17
Extinction	0.076(3)	0.147(5)	0.127(5)	0.048(3)	0.072(3)	0.036(2)	0.016(1)	0.017(2)	0.023(2)	0.017(1)	0.027(2)	0.012(2)	0.020(2)

timated from the extinction parameter (BECKER and COPPENS, 1974; GERING, 1985) varies significantly even in the untreated natural sample from domain to domain (samples 1.a and 1.b in Tab. 3). Prolonged heating at 750 °C and subsequent quenching (samples 2.a and 2.b in Tab. 3) did not lead to a drastic reduction of crystal perfection. A similar effect was also observed for 3 h heating at 950° and subsequent quenching. However, increased heating time (12–672 h) at 900°–950° and subsequent quenching (samples 4.a–7.b. in Tab. 3) yielded a strongly decreased and rather constant extinction coefficient of 0.019 within 4 e.s.d.'s. This behaviour indicates that the formation of mosaic

blocks (decreasing extinction) was not solely due to quenching from high temperature but due to long time heating and quenching. If we assume in accordance with previous studies (e.g., HARRIS et al., 1989; McLAREN and FITZ GERALD, 1987; XIAO et al., 1995) that natural Itrongay low-sanidine exhibits a modulated fine structure in the range of 100 Å, this tweed pattern seems not to reduce the empirical extinction coefficient as refined in the course of this single-crystal X-ray structure study. In other words, the individual tweed domains are very small "twin" domains (with increased degree of Si,Al order) but invisible for X-rays because they are smaller than the X-ray coherence length.

Tab. 4 Tetrahedral site occupancy factors of differently heated Itrongay K-feldspar.

#	time [h]	T [°C]	Electron density							
			t_1 calc. from b and c	t_1 calc. from <T-O>	observed T_1	observed T_2	calculated T_1	calculated T_2	differences observed – calculated T_1	differences observed – calculated T_2
1. a	0	0	0.352(6)	0.36(3)	13.61(6)	13.66(4)	13.6(1)	13.9(1)	0.0(1)	-0.2(1)
b	0	0	0.354(5)	0.36(3)	13.69(4)	13.71(4)	13.65(9)	13.85(9)	0.0(1)	-0.1(1)
2. a	336	750	0.35(1)	0.36(3)	13.58(8)	13.55(8)	13.7(2)	13.9(2)	-0.1(2)	-0.4(2)
b	672	750	0.356(8)	0.35(3)	13.59(8)	13.65(8)	13.6(2)	13.9(2)	0.0(2)	-0.3(2)
3. a	3	950	0.352(6)	0.35(3)	13.66(4)	13.68(4)	13.6(1)	13.9(1)	0.1(1)	-0.2(1)
b	3	950	0.352(4)	0.36(3)	13.72(4)	13.73(4)	13.65(8)	13.85(8)	0.07(9)	-0.12(9)
4. a	12	950	0.351(4)	0.35(3)	13.66(6)	13.68(6)	13.65(8)	13.85(8)	0.0(1)	-0.2(1)
b	12	950	0.350(4)	0.35(3)	13.65(6)	13.69(6)	13.65(8)	13.85(8)	0.0(1)	-0.2(1)
5	12	950	0.351(4)	0.36(3)	13.58(6)	13.65(6)	13.65(8)	13.85(8)	-0.1(1)	-0.2(1)
6. a	18	950	0.343(8)	0.35(3)	13.59(6)	13.64(6)	13.7(2)	13.8(2)	-0.1(2)	-0.2(2)
b	18	950	0.334(6)	0.34(3)	13.19(4)	13.33(4)	13.7(1)	13.8(1)	-0.5(1)	-0.5(1)
7. a	672	900	0.318(5)	0.32(3)	13.47(6)	13.55(6)	13.68(9)	13.82(9)	-0.2(1)	-0.3(1)
b	672	900	0.273(7)	0.27(3)	13.90(6)	13.96(6)	13.7(1)	13.8(1)	0.2(1)	0.2(1)0

All site occupancies were calculated:

a) based on unit cell dimensions: $2t_1 = -7.590 - 2.3258 \cdot \mathbf{b} + 5.3581 \cdot \mathbf{c}$

b) based on the average T-O bond lengths: $t_1 = 0.25 + [(<T_1-O> - <<T-O>>)/0.125]$

Observed electron densities are directly from crystal structure refinement assuming pure Si on all T-sites

Calculated electron densities = $[(1-t_1) \cdot 14] + [t_1 \cdot 13]$

It may be suggested that the modulation compensates for structural stress and strain. With increasing heating time within the stability range of high-sanidine the tweed pattern coarsens until the crystal becomes finally homogeneous (high-sanidine) even on submicroscopic scale. Thus the increased strain is now compensated by formation of mosaic blocks (decrease of extinction).

The presence of structural defects such as a more pronounced mosaic pattern or even Fe/Al or Na/K inhomogeneities in the Itrongay K-feldspar could explain the observed variations of tetrahedral cation re-distribution in samples 7.a and 7.b, since the re-distribution of Al and Si in the tetrahedral sites is known to strongly depend on structural defects (LASAGA, 1981; GERING, 1985).

The presence of structural defects in reaction to heating is confirmed by non-ideal optical properties. PRIESS (1981) observed optical inhomogeneities in natural, untreated samples. When heated, these optical inhomogeneous areas changed the optic-axial angle which was interpreted by PRIESS (1981) as a transformation from an Si,Al ordered to disordered state, whereas optically homogeneous parts remained unaffected. No chemical differences between the differently reacting regions could be found (PRIESS, 1981). Also interference colors change very heterogeneously with heating in a specific area of observation, as described in COOMB'S study (1954). Although Itrongay K-feldspar is free of macroscopic twin and lamellar boundaries, it does not imply a defect-free state at a microscopic or nanoscopic scale (see also FOLAND, 1994 and VILLA, 1996).

The internal exchange processes targeted in this study only consider re-distribution of Si, Al, and Fe among T_1 and T_2 . For radiometric and trace

element kinetic investigations, other diffusion processes such as coarsening of the submicroscopic modulation, T_1 - T_1 , T_2 - T_2 diffusion, and diffusional jumps of (K, Na) in alkaline positions are of crucial importance but not analyzed in the present work. Thus, more detailed structural knowledge of Itrongay K-feldspar is required before trace element diffusion, such as Ar release studied in georadiometry, can be fully understood.

The Si,Al interdiffusion rate had usually been considered as a small perturbation on the scale of the typical Ar diffusion experiments. However, the energetics of Si,Al interdiffusion (223 ± 11.3 kJ/mole, according to KROLL and KNITTER, 1991) is indistinguishable at the 2-sigma level from that of Ar diffusion (189 ± 6.4 kJ/mole – recalculated on the basis of the data in VILLA [1996]). This may mean that the same physical phenomenon controls the mobility of Ar and Si,Al, Fe. To estimate the degree of Si,Al,Fe rearrangement, we have no direct determination, but we can argue as follows. The t_i parameter (see above) is 0.352 in the untreated material, and becomes 0.25 for complete statistical disorder (RIBBE, 1983). Thus our observed value $t_i = 0.273$ (for sample 7.b) approaches the (as yet undetermined) asymptotic steady state value for 900 °C by > 75%. The average t_i value of our two samples (7.a and 7.b) is 0.295, ca 55% of the way towards complete Si,Al,Fe disorder. Sample 6.b can similarly be said to have achieved $\geq 18 \pm 12\%$ of complete disorder. Concerning the Ar diffusivity, we obtained a bulk Ar loss of $12 \pm 1\%$ for the 18 h experiment (sample 6.b). We also analyzed a 0.7 mg chip from the surface of the same 672 h anneal at 900 °C and determined a bulk Ar loss of 70%. Both values are smaller than the highest corresponding Si,Al diffusion rates. In other words, Si,Al, Fe disordering

Tab. 4 (cont.)

#	time [h]	T [°C]	Si	T_1 Al	Final site occupancies			
					Fe	Si	T_2 Al	Fe
1. a	0	0	0.644(8)	0.331(8)	0.025	0.856(8)	0.144(8)	0
b	0	0	0.643(8)	0.332(8)	0.025	0.857(8)	0.143(8)	0
2. a	336	750	0.644(8)	0.331(8)	0.025	0.856(8)	0.144(8)	0
b	672	750	0.646(8)	0.329(8)	0.025	0.857(8)	0.143(8)	0
b	3	950	0.644(8)	0.331(8)	0.025	0.856(8)	0.144(8)	0
4. a	12	950	0.650(8)	0.325(8)	0.025	0.850(8)	0.150(8)	0
b	12	950	0.652(8)	0.323(8)	0.025	0.849(8)	0.151(8)	0
5	12	950	0.641(8)	0.334(8)	0.025	0.859(8)	0.141(8)	0
6. a	18	950	0.650(8)	0.325(8)	0.025	0.850(8)	0.150(8)	0
b	18	950	0.662(8)	0.326(8)	0.0125	0.838(8)	0.150(8)	0.0125
7. a	672	900	0.680(8)	0.307(8)	0.0125	0.819(8)	0.169(8)	0.0125
b	672	900	0.726(8)	0.262(8)	0.0125	0.774(8)	0.214(8)	0.0125

Tab. 5 Atomic coordinates and displacement parameters for a natural and a heated sample of Itrongay K-feldspar.

Sample	atom	x/a	y/b	z/c	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
1.a	K	0.21454(9)	1/2	0.3617(1)	0.0193(4)	0.0354(5)	0.0308(4)	0.0	0.0083(3)	0.0	0.0295(2)
Natural	T1	0.20960(6)	0.38208(4)	0.84434(8)	0.0117(3)	0.0099(3)	0.0132(3)	0.0000(2)	0.0050(2)	0.0003(2)	0.0118(2)
	T2	0.99054(6)	0.18506(4)	0.27612(7)	0.0132(3)	0.0133(3)	0.0126(3)	0.0012(2)	0.0060(2)	0.0022(2)	0.0129(2)
	O1	0.1389(3)	1/2	0.7854(4)	0.020(1)	0.013(1)	0.026(1)	0.0	0.0038(9)	0.0	0.0222(5)
	O2	0.3197(2)	0.3737(1)	0.0942(2)	0.0217(8)	0.0205(7)	0.0173(7)	0.0011(5)	0.0045(6)	0.0024(6)	0.0213(4)
	O3	0.0	0.1464(2)	1/2	0.026(1)	0.021(1)	0.021(1)	0.0	0.0112(9)	0.0	0.0221(5)
	O4	0.0350(2)	0.3111(1)	0.7585(2)	0.0180(8)	0.0181(8)	0.0233(7)	-0.0023(6)	0.0078(6)	-0.0018(6)	0.0203(4)
	O5	0.1723(2)	0.1470(1)	0.2728(3)	0.0229(8)	0.0320(9)	0.0266(8)	-0.0008(7)	0.0150(6)	0.0033(7)	0.0257(4)
7.b	K	0.2144(1)	1/2	0.3620(1)	0.0207(4)	0.0402(5)	0.0334(5)	0.0	0.0089(3)	0.0	0.0325(2)
762 h	T1	0.20902(6)	0.38203(4)	0.84413(8)	0.0112(3)	0.0097(3)	0.0122(3)	0.0001(2)	0.0044(2)	0.0006(2)	0.0113(2)
900 °C	T2	0.99063(7)	0.18504(4)	0.27650(7)	0.0119(3)	0.0123(3)	0.0100(3)	0.0010(2)	0.0051(2)	0.0021(2)	0.0113(2)
	O1	0.1368(3)	1/2	0.7849(4)	0.019(1)	0.015(1)	0.026(1)	0.0	0.0040(9)	0.0	0.0223(5)
	O2	0.3204(2)	0.3732(1)	0.0963(2)	0.0216(8)	0.0215(8)	0.0157(7)	0.0011(6)	0.0039(6)	0.0023(6)	0.0211(4)
	O3	0.0	0.1471(2)	1/2	0.027(1)	0.021(1)	0.017(1)	0.0	0.0112(9)	0.0	0.0212(5)
	O4	0.0341(2)	0.3100(1)	0.7573(2)	0.0183(7)	0.0177(8)	0.0232(7)	-0.0019(6)	0.0078(6)	-0.0012(6)	0.0202(4)
	O5	0.1711(2)	0.1467(1)	0.2732(3)	0.0212(8)	0.0323(9)	0.0260(8)	-0.0005(7)	0.0135(6)	0.0041(7)	0.0254(4)

Final structural-chemical formulas 1.a $(K_{0.95}Na_{0.05})[(Al_{0.662}Fe_{0.05}Si_{1.288})(Al_{0.288}Si_{1.712})]O_8$
 7.b $(K_{0.95}Na_{0.05})[(Al_{0.523}Fe_{0.025}Si_{1.452})(Al_{0.427}Fe_{0.025}Si_{1.548})]O_8$

rates are not slower than Ar diffusion. We are forced to conclude that the rate of Ar release is limited by the opening of the feldspar framework which requires T-O bond breaking, and thus occurs at similar activation energies as Si,Al diffusion and alkali cations (SMITH, 1974, Chapter 16). In turn, this has an important implication that the diffusion of Ar is not compatible with the physical basis of Fick's equations (movement of neutral species in an infinitely dilute solution) because the atom-atom interactions are dominant and require a quantum-mechanical treatment (MANNING, 1974). In addition, the hypothesis that diffusion of Ar on one hand, and Si, Al and Fe on the other hand are coupled with each other (i.e. that Ar enjoys no special status due to its "neutrality") can imply that where a plurality of pathways becomes available in a real crystal the transport of Ar atoms will take on the characteristics of multipath diffusion (VILLA, 1994). A further crucial observation is the variation of the t_l parameter between different crystal fragments. This shows that local kinetic effects predominated over a statistical steady state regime as would be required if Fick's law were a valid approximation. It is important to note that the functional form of the T-O bond breaking rate, i.e. its physical basis, is still an unsettled issue. SMITH (1974, Chapter 16) quotes studies favouring a Fickian rate law and studies favouring a second-order reaction rate law. As further pointed out by SMITH (1974), the dependence of the rate constant on grain size implies a decisive importance of surface-related kinetics.

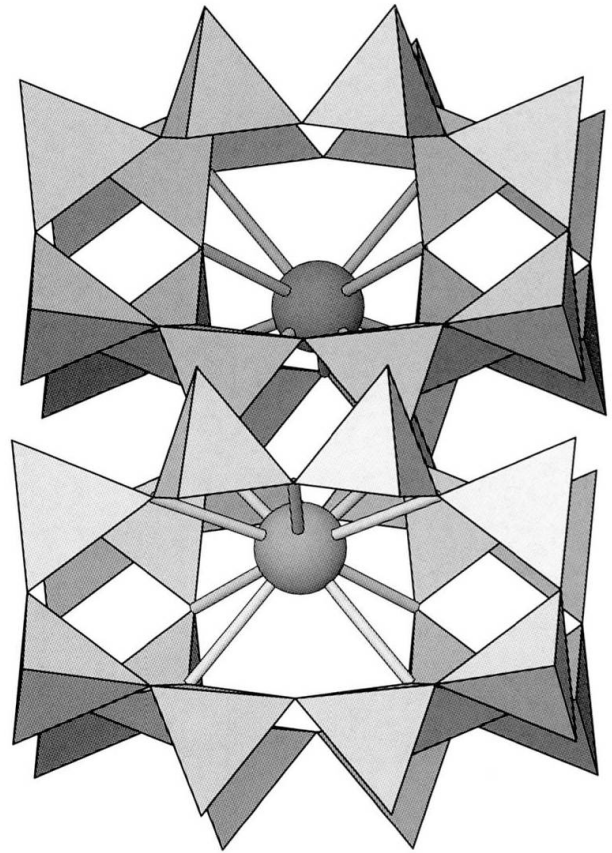


Fig. 1 (a) Tetrahedral framework of K-feldspar projected parallel to the a -axis (b is horizontal) elucidating the coordination of K. The largest access ports to the K site are formed by strongly compressed eight-membered rings of tetrahedra.

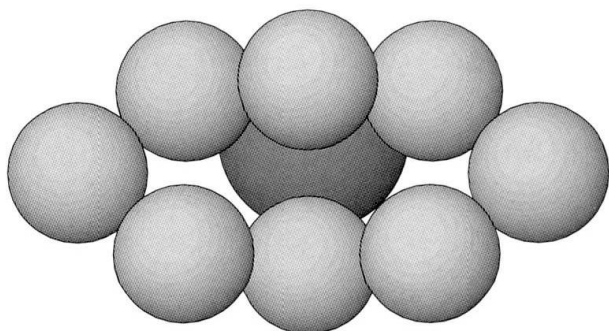


Fig. 1 (b) The limiting boundaries of the eight-membered rings of tetrahedra (Fig. 1a) are drawn assuming an oxygen ionic radius of 1.4 Å. A potential Ar atom (diameter 3.8 Å) is drawn as black sphere at the K position. It is obvious that Ar can not penetrate the strongly compressed eight-membered ring without T-O breaking.

Finally, support for our suggestion that Ar diffusion is rate limited by T-O breaking comes from tetrahedral framework geometry. Under high pressure conditions (6–10 kbar) and elevated temperature the spherical Ar atom with a diameter of ca 3.8 Å is able to penetrate fully expanded six-membered rings of the cordierite structure without apparent T-O bond breaking (ARMBRUSTER, 1985; SCHREYER et al., 1976). The high pressure condition, however, is important because compressibility data indicate that at 10 kbar the van der Waals diameter of Ar is reduced to 2.96 Å (SCHREYER et al., 1960). Thus this molecule may diffuse through a pinhole with a free aperture of ca 2.6 Å as found along the channel axis of cordierite. In case of K-feldspar, we assume that the most appropriate position for Ar are those sites normally occupied by K. The largest ports giving access to the K coordination polyhedra are limited by strongly compressed eight-membered rings of tetrahedra (Fig. 1) with a central O...O distance of 3.8 Å. If we consider an ionic radius for oxygen of 1.4 Å, the free aperture of the eight-membered rings reduces to a pinhole of ca. 1 Å diameter (Fig. 1) which is certainly too small to allow Ar (diameter 3.8 Å) to diffuse through such a narrow passage without T-O breaking.

Acknowledgements

The electron microprobe laboratory was supported by the Swiss National Science Foundation (credit # 21-26579.89), the University of Bern and the "Wander Stiftung". This study is part of the Ph.D. Thesis of Daniel Nyfeler, supported by the Swiss National Science Foundation (credit # 20-49733.96). The constructive review of M. Kunz is highly appreciated.

References

- ARMBRUSTER, TH. (1985): Ar, N₂, and CO₂ in the structural cavities of cordierite, an optical and X-ray single-crystal study. *Phys. Chem. Minerals*, 12, 233–245.
- ARNAUD, N.O. and KELLEY, S.P. (1997): Argon behaviour in gem-quality orthoclase from Madagascar: Experiments and some consequences for ⁴⁰Ar/³⁹Ar geochronology. *Geochim. Cosmochim. Acta*, 61, 3227–3255.
- BARTH, T. F.W. (1951): Permanent changes in the optical orientation of feldspars exposed to heat. *Norsk Geol. Tidsskrift*, 12, 57–72.
- BAILEY, S.W. (1969): Refinement of an intermediate microcline structure. *Amer. Mineral.*, 54, 1540–1545.
- BECKER, P.J. and COPPENS, P. (1974): Extinction within the limit of the Darwin transfer equations. I. General formalisms for primary and secondary extinction and their application to spherical crystals. *Acta Cryst. A30*, 129–147.
- CARMICHAEL, I.S.E. (1967): The mineralogy and petrology of the volcanic rocks from Leucite Hills, Wyoming. *Contrib. Mineral. Petrol.*, 15, 24–66.
- COLVILLE, A.A. and RIBBE, P.H. (1968): The crystal structure of an adularia and a refinement of the structure of orthoclase. *Amer. Mineral.*, 53, 25–37.
- COOMBS, D.S. (1954): Ferriferous orthoclase from Madagascar. *Mineral. Mag.*, 30, 409–427.
- FAYE, G.H. (1969): The optical absorption spectrum of tetrahedrally bonded Fe³⁺ in orthoclase. *Can. Mineral.*, 10, 112–117.
- FOLAND, K.A. (1994): Argon diffusion in feldspars. In: PARSON, I. (ed.): *Feldspars and their reactions*. 415–447. Kluwer Academic Publishers.
- GERING, E. (1985): Silizium/Aluminium-Ordnung und Kristallperfektion von Sanidinen. Ph.D. dissertation, Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe.
- HARRIS, M.J., SALJE, E.K.H., GÜTTLER, B.K. and CARPENTER, M.A. (1989): Structural states of natural potassium feldspar: an infrared spectroscopic study. *Phys. Chem. Minerals*, 16, 649–658.
- HEWLETT, C.G. (1959): Optical properties of potassic feldspars. *Geol. Soc. America, Bull.*, 70, 511–538.
- HOFMEISTER, A.M. and ROSSMAN, G.R. (1984): Determination of Fe²⁺ and Fe³⁺ concentrations in feldspar by optical absorption and EPR spectroscopy. *Phys. Chem. Minerals*, 11, 213–224.
- KROLL, H. and KNITTER, R. (1991): Al,Si exchange kinetics in sanidine and anorthoclase and modeling of rock cooling paths. *Amer. Mineral.*, 76, 928–941.
- KROLL, H. and RIBBE, P.H. (1983): Lattice parameters, composition and Al, Si order in alkali feldspars. In: *Reviews in Mineralogy, Feldspar Mineralogy* (ed.: RIBBE, P.H.), Vol. 2, second edition, Chap. 3, 57–99.
- KÔZU, S. and SUZUKI, M. (1925): The influence of temperature on the optic axial angle of adularia, yellow orthoclase and moonstone. *Sci. Rep. Tôhoku Univ.*, Ser. 3, 2, 187–201.
- LACROIX, A. (1912): Note préliminaire sur quelques minéraux de Madagascar dont plusieurs peuvent être utilisés comme gemmes. *Comptes Rendus de l'Académie des Sciences, Paris*, 155, 672–677.
- LASAGA, A.C. (1981): The atomistic basis of kinetics: defects in minerals. In: LASAGA, A.C. and KIRKPATRICK, R.J. (eds): *Kinetics of Geochemical Processes Rev. Mineralogy Vol. 8*, 261–319.
- MANNING, J.R. (1974): Diffusion kinetics and mechanisms in simple crystals. In: HOFMANN, A.W., GILETTI, B.J., YODER, H.S., and YUND, R.A. (eds): *Geo-*

- chemical Transport and Kinetics. Carnegie Institution of Washington Publication 634, 3–13.
- MCLAREN, A.C. and FITZ GERALD, J.D. (1987): CBED and ALCHEMI investigations of local symmetry and Al, Si ordering in K-feldspars. *Phys. Chem. Minerals*, 14, 281–292.
- NADEZHINA, T.N., PUSHCHAROVSKII, D.Y., TAROEV, V.K., TAUSON, V.L. and BYCHKOV, A.M. (1993): Crystal structure of the ferrialuminosilicate low sanidine. *Crystallographic Reports*, 38, 753–755.
- PETROV, I. and HAFNER, S.S. (1988): Location of trace Fe^{3+} ions in sanidine, KAlSi_3O_8 . *Amer. Mineral.*, 73, 97–104.
- PETROV, I., YUDE, F., BERSHOV, L.V., HAFNER, S.S. and KROLL, H. (1989): Order-disorder of Fe^{3+} ions over the tetrahedral positions in albite. *Amer. Mineral.*, 74, 604–609.
- PRIESS, U. (1981): Untersuchungen zur Tief-Hoch-Umwandlung von Fe-haltigen Orthoklas-Kristallen aus Madagaskar. *N. Jahrb. Mineral. Abh.*, 141(1), 17–29.
- RIBBE, P.H. (1974): A comparison of bonding effects in ussingite and low albite. *Amer. Mineral.*, 59, 341–344.
- RIBBE, P.H. (1983): Chemistry, structure and nomenclature of feldspars. In: RIBBE, P.H. (ed.): *Feldspar Mineralogy*. *Rev. Mineralogy* Vol. 2, 2nd ed., 1–20.
- SCHREYER, W., YODER, H.S. and ALDRICH, L.T. (1960): Synthesis of an argon-containing cordierite. *Ann. Rep. Dir. Geophys. Lab.*, 59, 94–96.
- SETO, K. (1923): Chemical study of some feldspars. *Sci. Rep. Tôhoku Univ.*, Ser. 3, 1, 219–231.
- SHELDRIK, G.M. (1993): SHELX-93. Program for crystal structure determination, University of Göttingen, Federal Republic of Germany.
- SMITH, J.V. (1974): *Feldspar Minerals*. 2. Chemical and Textural Properties. Springer.
- SPENCER, E. (1930): A contribution to the study of moonstone from Ceylon and other areas and of the stability relations of the alkali-feldspars. *Mineral. Mag.*, 29, 757–758.
- SPENCER, E. (1937): The potash-soda feldspars I. Thermal stability. *Mineral. Mag.*, 24, 453–494.
- STEWART, D.B. and RIBBE, P.H. (1983): Optical properties of feldspars. In: RIBBE, P.H. (ed.): *Feldspar Mineralogy*. *Rev. Mineralogy* Vol. 2, 2nd ed., 121–139.
- SU, S.C., BLOSS, F.D., RIBBE, P.H. and STEWART, D.B. (1984): Optic axial angle, a precise measure of Al, Si ordering in T_1 tetrahedral sites of K-rich alkali feldspars. *Amer. Mineral.*, 69, 440–448.
- TUTTLE, O.F. (1952): Optical studies on alkali feldspars. *Amer. J. Sci.*, Bowen Volume, 553–567.
- VILLA, I.M. (1994): Multipath Ar transport in K-feldspar deduced from isothermal heating experiments. *Earth Planet. Sci. Lett.*, 122, 393–401.
- VILLA, I.M. (1996): The influence of irradiation and heating schedule on Ar diffusion in gem-quality orthoclase from Madagascar. *V.M. Goldschmidt Conf.*, Heidelberg, Germany, 652.
- WALTHER, V. (1966): Der Orthoklas von Itrongay auf Madagaskar und seine Einordnung in das System der Kalifeldspäte. Ph.D. dissertation. Universität Hamburg.
- WONES, D.R. and APPLEMAN, D.E. (1961): X-ray crystallography and optical properties of synthetic monoclinic KFeSi_3O_8 iron-sanidine. *USGS Prof. Paper*, 424-C, C-309.
- WONES, D.R. and APPLEMAN, D.E. (1963): Properties of synthetic triclinic KFeSi_3O_8 iron-microcline, with some observations on the iron-microcline \leftrightarrow iron-sanidine transition. *J. Petrology*, 4, 131–137.
- XIAO, Y., KIRKPATRICK, J., HAY, R.L. and KIM, Y.J. (1995): Investigation of Al, Si order in K-feldspars using ^{27}Al and ^{29}Si MAS NMR. *Mineral. Mag.*, 59, 47–61.

Received September 2, 1997; revision accepted November 28, 1997.