

Raman spectroscopic characterisation of disordered alkali feldspars along the join KAlSi_3O_8 – $\text{NaAlSi}_3\text{O}_8$: application to natural sanidine and anorthoclase

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Abstract: This study reports a calibration of Raman band positions for the determination of the Na/K ratio in disordered alkali feldspars. Crystals along the join sanidine–anorthoclase were synthesised in steps of 10 mol% by ion exchange from a natural sanidine from Volkesfeld and were analysed by electron microprobe. Calibrations were made for the positions of three Raman bands located at 120–142 cm^{-1} (band A), 454–461 cm^{-1} (band B) and 510–514 cm^{-1} (band D) and for the difference between D and A (ΔDA). The calibrations for band A and ΔDA are most suitable for the determination of composition. They show two linear trends with an intersection at about $\text{K}/(\text{Na}+\text{K}) = 0.32$, which is probably due to the phase transition between the monoclinic and triclinic crystal structures of sanidine and anorthoclase, respectively. For anorthoclase ($\text{K}/(\text{Na}+\text{K}) < 0.32$) the Raman shift (RS) of band A is related to composition by $\text{K}/(\text{Na}+\text{K}) = 4.5077 - 0.0316 \cdot \text{RS}$. For sanidine ($\text{K}/(\text{Na}+\text{K}) > 0.32$) the correlation $\text{K}/(\text{Na}+\text{K}) = 7.3675 - 0.0550 \cdot \text{RS}$ was obtained. Both correlations allow the determination of $\text{K}/(\text{Na}+\text{K})$ with an accuracy of better than ± 0.04 for the synthetic anorthoclase and sanidine. The application of this calibration to natural samples was tested by analysing a series of alkali feldspars ($\text{K}/(\text{Na}+\text{K}) = 0.28 - 0.86$) from various volcanic rocks. These data suggest that the calibration can be used to estimate the $\text{K}/(\text{Na}+\text{K})$ ratio in natural disordered alkali feldspars with an accuracy of better than 0.1. A further improvement can be reached by using ΔDA , for which the correlations $\text{K}/(\text{Na}+\text{K}) = -8.3608 + 0.0228 \cdot \Delta\text{DA}$ and $\text{K}/(\text{Na}+\text{K}) = -21.5327 + 0.0573 \cdot \Delta\text{DA}$ were obtained for anorthoclase and sanidine, respectively. These correlations allow the determination of $\text{K}/(\text{Na}+\text{K})$ with an accuracy of about ± 0.03 for the synthetic anorthoclase and sanidine and ± 0.07 for the natural samples.

Key-words: Raman spectroscopy, alkali feldspar, composition.

1. Introduction

The high-temperature modifications of alkali feldspars ($\text{NaAlSi}_3\text{O}_8$ – KAlSi_3O_8) exhibit full solid solution and are common minerals in alkali-rich volcanic rocks such as rhyolites, phonolites or trachytes. The high-temperature phases sanidine (KAlSi_3O_8) and monalbite ($\text{NaAlSi}_3\text{O}_8$) are both monoclinic due to statistical (disordered) distribution of Al and Si on 4 different tetrahedral sites. While sanidine can be quenched to room temperature, monalbite undergoes a displacive monoclinic to triclinic phase transition at about 980 °C leading to analbite, but keeping the disordered Al–Si distribution. In the quenched solid-solution series the monoclinic to triclinic phase transformation occurs at room temperature at about 34–37 mol% sanidine component (Kroll *et al.*, 1986; Zhang *et al.*, 1996). Those fully disordered Na-rich feldspars, which may have possessed monoclinic symmetry at their formation temperature but became triclinic upon cooling, are called anorthoclase. At low temperatures alkali feldspars exhibit ordering of Al on one single tetrahedral site and tend to

unmix into Na-rich and K-rich feldspar phases. More details about nomenclature, crystal structures and unmixing of alkali feldspars can be found in reviews of Ribbe (1983), Kroll & Ribbe (1983) and Deer *et al.* (1992).

Previous Raman spectroscopic studies on alkali feldspars investigated primary Si–Al ordered or disordered end-members with the aim to provide a rapid and non-destructive tool for feldspar identification (Mernagh, 1991; Freeman *et al.*, 2003). McKeown (2005) obtained Raman spectra of albite from 25 °C to melting temperature and provided vibrational assignments with help of lattice dynamics calculations. Calculations of vibrational normal modes of various alkali feldspars were previously reported by von Stengel (1977). Raman spectroscopy was also used to study the displacive phase transition in anorthoclase (Salje, 1986).

Although Raman spectroscopy was previously applied to determine the composition of other silicate minerals such as olivines, garnets and pyroxenes (Guyot *et al.*, 1986; Mernagh & Hoatson, 1997; Huang *et al.*, 2000; Wang *et al.*, 2001, 2004; Smith, 2005; Kuebler *et al.*,

2006; Stalder *et al.*, 2008), no such attempts were made for alkali feldspars. The aim of this study was the systematic Raman spectroscopic investigation of a series of synthetically prepared, disordered alkali feldspars along the join sanidine – analbite, with the particular focus on providing a tool for the determination of the Na/K ratio in these minerals. The application of the obtained calibration to natural samples was tested by measuring Raman spectra of alkali feldspars from various volcanic rocks.

2. Mineral synthesis and analysis

Crystals of the analbite – high sanidine series were synthesised following the method described in Kroll *et al.* (1986). The end-members sanidine and analbite were produced from a natural gem-quality sanidine megacryst from Volkesfeld by ion exchange at about 850 °C in molten KCl and NaCl, respectively. For this purpose the crystal was crushed and 2 g of sanidine fragments of the grain size between 63 and 250 µm were mixed with 40 g of KCl or NaCl. The mixtures were filled into alumina crucibles, covered with a lid and were placed into tube furnaces at about 850 °C for 20 h. Subsequently, the salt was dissolved in H₂O and the remaining feldspar crystals were thoroughly rinsed in deionised H₂O to remove traces of salt. The experiment in molten NaCl was repeated once to ensure complete ion exchange. After these treatments the crystals were full of fractures along cleavage planes, leading to a reduction of the initial grain size. Mixtures of the end-members in steps of 10 mol% were homogenised in an agate mortar, pressed to pellets in a hydraulic press and were then placed in a box furnace at 1 atm and 1000 °C. After 3 days of sintering, the samples were removed from the furnace, re-ground for further homogenisation and pressed again into pellets to repeat the sintering process for three more days. After this procedure most crystals of the final feldspars were smaller than 20 µm, but several crystals of 50–100 µm in size could be recovered from every charge.

In order to compare naturally formed alkali feldspars with the synthetic series, several volcanic rocks containing sanidine or anorthoclase as phenocrysts or inclusions (rhyolite from Gleichenberg, Austria (RG); trachyte from Drachenfels, Germany (TDF); phonolite from Roche en Regnier, France (PRR); mafic phonolite from Rieden, Germany (MPR); sanidine cumulate from Eifel, Germany (SCE) and basalt from Hoher Hagen, Germany (BHH)) were crushed and alkali feldspar crystal fragments were handpicked under a stereo microscope. In addition, the untreated sanidine from Volkesfeld, Germany (SVF) was also studied.

The chemical compositions of the synthetic and natural crystals were determined by electron microprobe (EMP) analysis. Oriented crystals (parallel to the cleavage plane (001)) and randomly orientated grains were embedded in epoxy resin, polished and analysed with a JEOLTM JXA 8900 RL electron microprobe using an accelerating

voltage of 15 kV, a beam current of 15 nA and a defocused beam of 10 µm in diameter. In the case of oriented crystals (natural feldspars), each sample was measured on 2–5 different spots; in the case of the synthetic series, 6–10 different crystals of every composition were analysed to check for homogeneity (one analysis per crystal). The results of the EMP analyses of the synthetic feldspar series are listed in Table 1, those of the natural samples are given in Table 2. The analysis of the synthetic feldspar series shows that the ion-exchange procedures produced mainly homogenous crystals. Only samples San30, San40 and San50 show larger variations in Na₂O and K₂O contents. The analyses also show that the initial sanidine from Volkesfeld, and therefore the synthetic samples, are nearly free of CaO, but contain ~0.9 wt% BaO and ~0.15 wt% SrO, resulting in about 0.0, 1.6 and 0.4 mol% anorthite (An), celsian (Cn) and Sr-feldspar (Sr-Fsp) components, respectively (Table 1). The natural feldspars (including the sanidine from Volkesfeld) show larger variations in these mineral components, which range from 0.0 to 9.4 mol% An, 0.0–1.6 mol% Cn and 0.0–2.2 mol% Sr-Fsp components (Table 2).

For the natural feldspars, the EMP samples were re-polished to remove the carbon coating along with the uppermost micrometers of sample, before Raman spectra were recorded. Furthermore, the Raman spectra were not obtained from exactly the same locations that were used for EMP analysis. For the synthetic series crystals other than those used for EMP analysis were analysed by Raman spectroscopy. Therefore, it can be ruled out that Raman spectra are affected by beam damage from EMP measurements. Raman spectra were collected from clean surfaces (mainly from the cleavage plane (001)), several micrometers away from crystal edges or fractures.

Raman measurements were performed using a confocal Horiba Jobin Yvon HR 800 UV Raman spectrometer with attached microscope (Olympus BX41). The use of the 488 nm excitation of an air cooled Ar⁺-laser (polarised beam with 25 mW at the laser exit, corresponding to ~6 mW at the sample), a holographic grating with 2400 lines/mm, and a Peltier cooled CCD detector with 1024 × 256 pixels, yielded a spectral dispersion of better than 0.43 cm⁻¹ per pixel (corresponding to a spectral resolution of better than 1.5 cm⁻¹). The lateral resolution was on the order of ~1 µm and the depth resolution was determined at ±7 µm. Raman spectra were measured in the range 80–850 cm⁻¹ with an acquisition of two times 60 s for each spectral window to enhance signal to noise and to remove spikes from the spectrum. For each synthetic sample, Raman spectra of at least five different crystals were measured. Between two samples the Raman spectrum of silicon was measured as a standard for peak position (Si band at 520.4 cm⁻¹). The absolute wavenumber accuracy of the HR 800 UV system is ±0.5 cm⁻¹, the wavenumber precision (±0.3 cm⁻¹) was determined from repeated measurements of the silicon standard against the Rayleigh line. The linearity of the spectrometer was calibrated against excitation lines of Ne.

Table 1. Electron microprobe analyses and positions of Raman bands A–D for the synthetic alkali feldspar series.

	San0 <i>n</i> = 10	San10 <i>n</i> = 7	San20 <i>n</i> = 6	San30 <i>n</i> = 6	San40 <i>n</i> = 7	San50 <i>n</i> = 7	San60 <i>n</i> = 7	San70 <i>n</i> = 7	San80 <i>n</i> = 8	San90 <i>n</i> = 6	San100 <i>n</i> = 10
<i>oxides (wt%)</i>											
SiO ₂	67.95 (0.13)	67.66 (0.16)	67.06 (0.13)	66.72 (0.25)	66.45 (0.15)	65.93 (0.24)	65.64 (0.12)	65.47 (0.14)	65.26 (0.08)	64.83 (0.21)	64.32 (0.14)
Al ₂ O ₃	19.72 (0.10)	19.64 (0.10)	19.42 (0.10)	19.34 (0.12)	19.31 (0.09)	19.15 (0.16)	19.13 (0.12)	19.03 (0.09)	18.95 (0.13)	18.78 (0.10)	18.74 (0.09)
FeO	0.15 (0.01)	0.15 (0.02)	0.15 (0.01)	0.16 (0.02)	0.14 (0.02)	0.14 (0.01)	0.16 (0.01)	0.14 (0.01)	0.15 (0.02)	0.14 (0.01)	0.14 (0.01)
CaO	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)	0.01 (0.01)	0.00 (0.01)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.01 (0.01)
SrO	0.15 (0.03)	0.16 (0.02)	0.16 (0.02)	0.13 (0.04)	0.14 (0.04)	0.12 (0.03)	0.15 (0.03)	0.14 (0.03)	0.15 (0.04)	0.11 (0.04)	0.14 (0.04)
BaO	0.92 (0.07)	0.92 (0.04)	0.95 (0.03)	0.95 (0.05)	0.91 (0.03)	0.89 (0.07)	0.87 (0.05)	0.90 (0.05)	0.87 (0.08)	0.83 (0.08)	0.89 (0.05)
Na ₂ O	11.50 (0.15)	10.38 (0.12)	9.05 (0.18)	7.77 (0.32)	6.70 (0.25)	5.26 (0.45)	4.46 (0.13)	3.13 (0.14)	2.22 (0.04)	1.11 (0.04)	0.03 (0.02)
K ₂ O	0.11 (0.09)	1.85 (0.03)	3.64 (0.11)	5.51 (0.47)	7.10 (0.31)	9.17 (0.71)	10.30 (0.17)	12.18 (0.27)	13.53 (0.11)	15.13 (0.07)	16.70 (0.08)
totals	100.50 (0.19)	100.76 (0.23)	100.43 (0.27)	100.58 (0.23)	100.75 (0.21)	100.66 (0.18)	100.69 (0.18)	100.98 (0.16)	101.13 (0.13)	100.93 (0.29)	100.97 (0.18)
<i>mineral components (mole%)</i>											
Or	0.6 (0.5)	10.3 (0.2)	20.5 (0.8)	31.2 (2.7)	40.3 (1.8)	52.4 (4.0)	59.2 (1.1)	70.5 (1.3)	78.5 (0.4)	88.4 (0.4)	97.7 (0.2)
Ab	97.4 (0.5)	87.7 (0.3)	77.4 (0.8)	66.8 (2.7)	57.7 (1.9)	45.7 (4.0)	38.9 (1.1)	27.5 (1.2)	19.5 (0.4)	9.8 (0.3)	0.3 (0.2)
An	0.0 (0.0)	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.1)
Cn	1.6 (0.1)	1.6 (0.1)	1.6 (0.1)	1.7 (0.1)	1.6 (0.1)	1.6 (0.1)	1.5 (0.1)	1.6 (0.1)	1.6 (0.1)	1.5 (0.1)	1.6 (0.1)
Sr-Fsp	0.4 (0.1)	0.4 (0.1)	0.4 (0.1)	0.3 (0.1)	0.4 (0.1)	0.3 (0.1)	0.4 (0.1)	0.4 (0.1)	0.4 (0.1)	0.3 (0.1)	0.4 (0.1)
K/(Na+K)-100	0.7 (0.2)	10.5 (0.2)	20.9 (0.8)	31.8 (2.8)	41.2 (1.9)	53.4 (4.6)	60.3 (1.1)	71.9 (1.3)	80.1 (0.4)	90.0 (0.3)	99.7 (0.2)
<i>Raman shift (cm⁻¹)</i>	<i>c</i> = 10	<i>c</i> = 6	<i>c</i> = 7	<i>c</i> = 5	<i>c</i> = 5	<i>c</i> = 5	<i>c</i> = 5	<i>c</i> = 5	<i>c</i> = 5	<i>c</i> = 7	<i>c</i> = 10
Band A (fit)	142.3 (1.0)	139.7 (0.8)	136.6 (1.0)	132.5 (0.8)	130.8 (0.8)	129.3 (0.7)	127.9 (0.8)	126.0 (0.7)	124.2 (0.8)	122.7 (0.8)	120.2 (0.8)
Band B (fit)	467.0 (3.1)	466.6 (3.8)	464.3 (3.3)	460.8 (1.0)	459.6 (1.0)	458.2 (0.7)	457.5 (0.7)	456.3 (0.7)	455.7 (0.7)	455.0 (0.7)	454.2 (0.8)
Band C (fit)	479.0 (0.8)	476.9 (0.9)	476.6 (0.9)	474.1 (0.8)	473.7 (0.8)	473.6 (0.7)	474.0 (0.7)	474.1 (0.7)	474.6 (0.7)	475.0 (0.8)	475.2 (0.8)
Band D (fit)	510.2 (0.8)	511.0 (0.7)	512.8 (0.8)	513.8 (0.8)	514.1 (0.7)	514.2 (0.7)	514.4 (0.6)	514.2 (0.7)	514.1 (0.7)	514.0 (0.7)	513.7 (0.7)
ΔDA (fit)	367.9 (1.0)	371.3 (0.7)	376.2 (1.1)	381.3 (0.8)	383.3 (0.8)	384.9 (0.6)	386.5 (0.6)	388.2 (0.6)	389.9 (0.6)	391.3 (0.7)	393.5 (0.7)
Band A (man. adjust.)	142.1 (1.3)	139.2 (0.9)	136.3 (1.0)	132.4 (0.9)	130.8 (0.8)	129.4 (0.7)	128.2 (0.7)	126.1 (0.8)	124.2 (0.7)	122.8 (0.8)	120.4 (0.9)
Band D (man. adjust.)	510.0 (0.8)	510.9 (0.7)	512.7 (0.8)	513.8 (0.8)	514.0 (0.7)	514.1 (0.7)	514.3 (0.6)	514.1 (0.7)	514.0 (0.6)	513.9 (0.8)	513.6 (0.7)
ΔDA (man. adjust.)	367.9 (1.3)	371.7 (0.8)	376.4 (1.0)	381.4 (0.9)	383.2 (0.8)	384.7 (0.6)	386.1 (0.6)	388.0 (0.7)	389.8 (0.6)	391.1 (0.8)	393.2 (0.8)

n: Number of microprobe analyses. Numbers in parentheses are the standard deviations of the different EMP analyses.

c: Number of crystals used to collect Raman spectra (one spectrum per crystal). The errors in Raman shifts for bands A–D were determined by error propagation from the standard deviations of the peak position measurements, the inaccuracy in absolute position of the Raman spectrometer ($\pm 0.5 \text{ cm}^{-1}$) and the precision of the Raman measurements ($\pm 0.3 \text{ cm}^{-1}$). The numbers were always rounded to the next higher decimal. The error in ΔDA was calculated by error propagation using the standard deviations for bands A and D and the precision of the Raman measurements (the inaccuracy in absolute position does not affect this number).

Table 2. Electron microprobe analyses and positions of Raman bands A–D for the natural alkali feldspars.

	Trachyte Drachenfels (TDF)			Sanidine Volkesfeld (SVF)				Sanidine cumulate (SCE)			
	TDF crystal #1 <i>n</i> = 5	TDF crystal #2 <i>n</i> = 5	TDF crystal #3 <i>n</i> = 5	SVF crystal #1 <i>n</i> = 5	SVF crystal #2 <i>n</i> = 5	SVF crystal #3 <i>n</i> = 5	SVF crystal #4 <i>n</i> = 5	SCE crystal #1 <i>n</i> = 5	SCE crystal #2 <i>n</i> = 5	SCE crystal #3 <i>n</i> = 5	SCE crystal #4 <i>n</i> = 5
<i>oxides (wt%)</i>											
SiO ₂	65.00 (0.16)	65.78 (0.39)	65.22 (0.16)	64.43 (0.14)	64.63 (0.09)	64.89 (0.23)	64.89 (0.36)	64.70 (0.32)	64.92 (0.19)	64.75 (0.24)	64.68 (0.31)
Al ₂ O ₃	19.03 (0.16)	19.25 (0.10)	19.14 (0.09)	18.69 (0.08)	18.76 (0.08)	18.80 (0.06)	18.76 (0.13)	19.61 (0.14)	19.70 (0.08)	19.63 (0.08)	19.61 (0.11)
FeO	0.16 (0.01)	0.16 (0.02)	0.15 (0.02)	0.14 (0.01)	0.14 (0.01)	0.14 (0.01)	0.14 (0.01)	0.20 (0.02)	0.21 (0.03)	0.21 (0.01)	0.20 (0.01)
CaO	0.44 (0.03)	0.56 (0.06)	0.40 (0.02)	0.00 (0.00)	0.00 (0.00)	0.00 (0.01)	0.00 (0.00)	0.88 (0.12)	0.94 (0.08)	0.95 (0.07)	0.92 (0.08)
SrO	0.14 (0.03)	0.12 (0.02)	0.15 (0.02)	0.14 (0.03)	0.17 (0.01)	0.14 (0.05)	0.14 (0.05)	0.09 (0.01)	0.12 (0.03)	0.14 (0.03)	0.11 (0.02)
BaO	0.65 (0.06)	0.56 (0.01)	0.89 (0.03)	0.90 (0.04)	0.90 (0.03)	0.87 (0.05)	0.88 (0.03)	0.23 (0.02)	0.20 (0.04)	0.25 (0.04)	0.23 (0.05)
Na ₂ O	3.97 (0.11)	5.17 (0.16)	3.94 (0.09)	1.64 (0.04)	1.59 (0.03)	1.59 (0.06)	1.59 (0.04)	4.15 (0.15)	4.13 (0.10)	4.14 (0.09)	4.14 (0.09)
K ₂ O	10.53 (0.14)	8.65 (0.27)	10.48 (0.08)	14.33 (0.07)	14.37 (0.12)	14.34 (0.09)	14.25 (0.08)	10.31 (0.33)	10.14 (0.21)	10.07 (0.14)	10.10 (0.18)
totals	99.91 (0.46)	100.26 (0.39)	100.35 (0.27)	100.27 (0.26)	100.55 (0.27)	100.79 (0.26)	100.65 (0.44)	100.16 (0.30)	100.36 (0.17)	100.12 (0.24)	99.98 (0.39)
<i>mineral components (mole%)</i>											
Or	61.3 (0.6)	50.3 (1.6)	61.2 (0.6)	83.5 (0.3)	83.9 (0.1)	83.9 (0.6)	83.9 (0.3)	59.0 (1.8)	58.5 (1.2)	58.2 (0.9)	58.5 (1.0)
Ab	35.1 (0.8)	45.7 (1.3)	34.9 (0.7)	14.5 (0.3)	14.1 (0.2)	14.2 (0.5)	14.2 (0.4)	36.1 (1.2)	36.3 (0.9)	36.3 (0.6)	36.4 (0.6)
An	2.1 (0.1)	2.7 (0.3)	1.9 (0.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	4.2 (0.6)	4.6 (0.4)	4.6 (0.3)	4.5 (0.4)
Cn	1.2 (0.1)	1.0 (0.0)	1.6 (0.1)	1.6 (0.1)	1.6 (0.1)	1.6 (0.1)	1.6 (0.1)	0.4 (0.0)	0.4 (0.1)	0.5 (0.1)	0.4 (0.1)
Sr-Fsp	0.4 (0.1)	0.3 (0.0)	0.4 (0.1)	0.4 (0.1)	0.4 (0.0)	0.4 (0.1)	0.4 (0.1)	0.2 (0.0)	0.3 (0.1)	0.4 (0.1)	0.3 (0.1)
K/(Na+K)·100	63.6 (0.8)	52.4 (1.5)	63.7 (0.7)	85.2 (0.3)	85.6 (0.2)	85.6 (0.5)	85.5 (0.4)	62.0 (1.5)	61.8 (1.0)	61.6 (0.8)	61.6 (0.8)
<i>Raman shift (cm⁻¹)</i>											
Band A (fit)	127.3 (0.6)	128.8 (0.7)	127.1 (0.6)	123.3 (0.6)	123.1 (0.6)	123.3 (0.6)	123.2 (0.6)	128.9 (0.6)	128.1 (0.6)	127.8 (0.6)	127.9 (0.6)
Band B (fit)	457.5 (0.6)	457.8 (0.7)	456.7 (0.6)	455.2 (0.6)	455.2 (0.6)	455.3 (0.6)	455.3 (0.6)	458.1 (0.6)	458.8 (0.6)	458.2 (0.6)	458.3 (0.6)
Band C (fit)	474.3 (0.6)	474.4 (0.7)	473.5 (0.6)	474.6 (0.6)	474.6 (0.6)	474.8 (0.6)	474.7 (0.6)	474.4 (0.6)	474.6 (0.6)	474.4 (0.6)	474.5 (0.6)
Band D (fit)	514.4 (0.6)	514.2 (0.6)	514.3 (0.6)	514.0 (0.6)	514.0 (0.6)	514.1 (0.6)	514.1 (0.6)	514.3 (0.6)	514.3 (0.6)	514.2 (0.6)	514.3 (0.6)
ΔDA (fit)	387.1 (0.5)	386.4 (0.6)	387.2 (0.5)	390.7 (0.5)	390.9 (0.5)	390.8 (0.5)	390.9 (0.5)	386.4 (0.5)	386.2 (0.5)	386.4 (0.5)	386.4 (0.5)
Band A (man. adjust.)	127.6 (0.6)	128.5 (0.8)	127.4 (0.6)	123.2 (0.6)	123.3 (0.6)	123.4 (0.6)	123.3 (0.6)	128.6 (0.6)	128.8 (0.6)	128.3 (0.6)	128.6 (0.6)
Band D (man. adjust.)	514.3 (0.6)	514.1 (0.7)	514.2 (0.6)	513.9 (0.6)	513.9 (0.6)	514.1 (0.6)	514.0 (0.6)	514.2 (0.6)	514.2 (0.6)	514.2 (0.6)	514.2 (0.6)
ΔDA (man. adjust.)	386.7 (0.5)	385.6 (0.7)	386.8 (0.5)	390.7 (0.5)	390.6 (0.5)	390.7 (0.5)	390.7 (0.5)	385.6 (0.5)	385.4 (0.5)	385.9 (0.5)	385.6 (0.5)

Table 2. Continued.

	Anorthoclase Basalt Hoher Hagen (BHH)		Rhyolite Gleichenberg (RG)		Mafic phonolithe, Eifel (MPR)		Phonolithe Roche en Regnier (PRR)	
	BHH crystal #1 <i>n</i> = 5	BHH crystal #2 <i>n</i> = 5	RG crystal #1 <i>n</i> = 2	RG crystal #2 <i>n</i> = 3	MPR crystal #1 <i>n</i> = 2	MPR crystal #2 <i>n</i> = 2	PRR crystal #1 <i>n</i> = 2	MPR crystal #2 <i>n</i> = 2
<i>oxides (wt%)</i>								
SiO ₂	64.07 (0.18)	64.29 (0.18)	65.92 (0.11)	66.06 (0.38)	64.74 (0.25)	65.20 (0.10)	66.07 (0.12)	66.80 (0.64)
Al ₂ O ₃	20.93 (0.16)	21.07 (0.14)	18.81 (0.22)	18.75 (0.15)	18.89 (0.15)	18.70 (0.18)	19.33 (0.13)	18.97 (0.08)
FeO	0.15 (0.02)	0.17 (0.01)	0.08 (0.02)	0.09 (0.01)	0.18 (0.02)	0.17 (0.02)	0.13 (0.02)	0.04 (0.01)
CaO	1.94 (0.07)	1.96 (0.02)	0.21 (0.03)	0.16 (0.02)	0.03 (0.02)	0.03 (0.01)	0.49 (0.02)	0.13 (0.01)
SrO	0.85 (0.07)	0.80 (0.04)	0.04 (0.01)	0.02 (0.01)	0.34 (0.02)	0.17 (0.07)	0.05 (0.04)	0.01 (0.01)
BaO	0.25 (0.03)	0.21 (0.02)	0.40 (0.08)	0.33 (0.02)	0.72 (0.05)	0.29 (0.31)	0.15 (0.02)	0.01 (0.02)
Na ₂ O	7.29 (0.05)	7.13 (0.10)	3.42 (0.02)	3.22 (0.08)	3.21 (0.12)	3.24 (0.01)	6.31 (0.07)	5.47 (0.11)
K ₂ O	4.44 (0.04)	4.61 (0.07)	11.74 (0.06)	11.98 (0.11)	11.99 (0.01)	12.05 (0.11)	7.60 (0.18)	9.29 (0.19)
Totals	99.90 (0.33)	100.24 (0.34)	100.61 (0.35)	100.62 (0.49)	100.10 (0.52)	99.86 (0.40)	100.13 (0.06)	100.71 (0.82)
<i>mineral components (mole%)</i>								
Or	25.2 (0.1)	26.3 (0.3)	68.1 (0.2)	70.0 (0.7)	69.4 (0.8)	70.2 (0.5)	43.0 (0.3)	52.4 (1.0)
Ab	62.9 (0.4)	61.8 (0.4)	30.1 (0.1)	28.6 (0.7)	28.2 (0.8)	28.7 (0.2)	54.3 (0.3)	46.9 (1.1)
An	9.3 (0.3)	9.4 (0.1)	1.0 (0.2)	0.8 (0.1)	0.2 (0.1)	0.1 (0.0)	2.3 (0.1)	0.6 (0.1)
Cn	0.4 (0.1)	0.4 (0.0)	0.7 (0.2)	0.6 (0.0)	1.3 (0.1)	0.5 (0.6)	0.3 (0.0)	0.0 (0.0)
Sr-Fsp	2.2 (0.2)	2.1 (0.1)	0.1 (0.0)	0.1 (0.0)	0.9 (0.0)	0.5 (0.2)	0.1 (0.1)	0.0 (0.0)
K/(Na+K)·100	28.6 (0.2)	29.8 (0.4)	69.3 (0.0)	71.0 (0.7)	71.1 (0.8)	71.0 (0.3)	44.2 (0.3)	52.8 (1.0)
<i>Raman shift (cm⁻¹)</i>								
Band A (fit)	<i>s</i> = 1 134.5 (0.6)	<i>s</i> = 1 132.8 (0.6)	<i>s</i> = 2 126.1 (0.6)	<i>s</i> = 2 125.8 (0.7)	<i>s</i> = 2 125.9 (0.6)	<i>s</i> = 2 125.8 (0.8)	<i>s</i> = 5 129.0 (1.3)	<i>s</i> = 1 128.9 (0.6)
Band B (fit)	465.0 (0.6)	468.8 (0.6)	456.2 (0.6)	456.1 (0.7)	456.4 (0.6)	456.4 (0.7)	458.5 (0.8)	457.0 (0.6)
Band C (fit)	475.9 (0.6)	475.8 (0.6)	473.9 (0.6)	473.8 (0.6)	474.1 (0.6)	474.1 (0.6)	475.4 (0.7)	475.3 (0.6)
Band D (fit)	512.9 (0.6)	513.2 (0.6)	514.3 (0.6)	514.3 (0.6)	514.3 (0.6)	514.3 (0.6)	513.8 (0.7)	513.9 (0.6)
ΔDA (fit)	378.4 (0.5)	380.4 (0.5)	388.2 (0.5)	388.5 (0.6)	388.4 (0.5)	388.5 (0.6)	384.8 (1.3)	385.0 (0.5)
Band A (man. adjust.)	134.6 (0.6)	133.0 (0.6)	125.9 (0.6)	126.0 (0.8)	125.7 (0.7)	126.0 (0.7)	130.7 (1.7)	129.0 (0.6)
Band D (man. adjust.)	512.8 (0.6)	513.1 (0.6)	514.2 (0.6)	514.2 (0.6)	514.2 (0.6)	514.3 (0.6)	513.8 (0.7)	513.9 (0.6)
ΔDA (man. adjust.)	378.2 (0.5)	380.1 (0.5)	388.3 (0.5)	388.2 (0.6)	388.5 (0.5)	388.3 (0.6)	383.1 (1.7)	384.9 (0.5)

n: Number of microprobe analyses. Numbers in parentheses are the standard deviation of the different EMP analyses.

s: Number of spectra collected for each crystal. In case of samples where 2 spectra were collected, the errors in Raman shifts for bands A–D were determined by error propagation from the standard deviations of the peak position measurements, the inaccuracy in absolute position of the Raman spectrometer ($\pm 0.5 \text{ cm}^{-1}$) and the precision of the Raman measurements ($\pm 0.3 \text{ cm}^{-1}$). The numbers were always rounded to the next higher decimal. For samples where only one spectrum was collected, the errors in Raman shift for bands A–D correspond to the error propagation of the inaccuracy in absolute position of the Raman spectrometer ($\pm 0.5 \text{ cm}^{-1}$) and the precision of the Raman measurements ($\pm 0.3 \text{ cm}^{-1}$). The error in ΔDA was calculated by error propagation using the standard deviations for bands A and D and the precision of the Raman measurements (the inaccuracy in absolute position does not affect this number).

3. Spectra evaluation

Figure 1 shows Raman spectra of the synthetic analbite-sanidine series in steps of 20 mol% sanidine component. The Raman modes, which occur at Raman shifts below 350 cm^{-1} are related to tetrahedral cage shear, modes between 350 and 550 cm^{-1} are related to 4-membered ring breathing deformation and modes between 550 and 850 cm^{-1} are related to tetrahedral deformation (McKeown, 2005). There occur also modes at wavenumbers between 1000 and 1200 cm^{-1} , which are caused by tetrahedral breathing. The latter range was not measured in this study because these bands are too broad and too low in intensity to be used for a calibration. Ideally, a suitable Raman band should have a high intensity and a narrow peak width, should not be affected by overlap with neighbouring bands, should be independent of orientation and largely dependent on chemical composition. After visual inspection of the Raman spectra, four bands were identified as possible candidates for a correlation of Raman peak position with chemical composition: band A exhibits the strongest compositional dependence, ranging in the synthetic sanidine – analbite series from about 120 to 142 cm^{-1} . Although this band is not very intense and is orientation-dependent, it seems to be most applicable to relate the Raman band position to the chemical composition. Band A appears most prominently in an orientation with the laser beam being focused on the cleavage plane (001), with the laser polarisation parallel to [010] (*i.e.* perpendicular to direction [100], which is the edge between the main cleavage planes (001) and (010)). The other bands chosen for evaluation are those, which compose the triplet in the wavenumber range 440 to 540 cm^{-1} and are denoted as bands B, C and D (Fig. 2). Although these bands may not be useful to determine the chemical composition over the entire range sanidine – analbite due to their limited compositional variations, bands B and D may be suitable

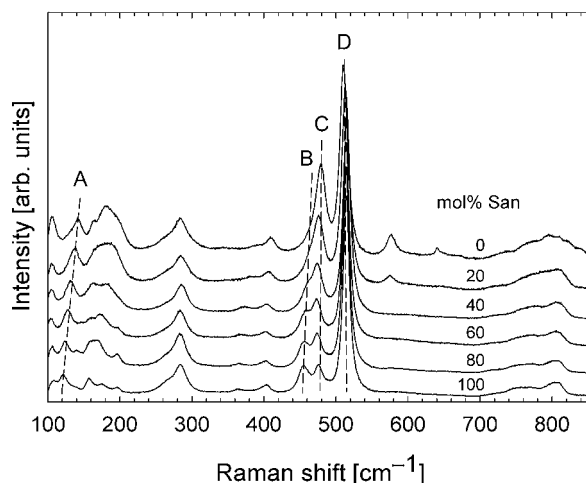


Fig. 1. Raman spectra of samples San0 (top) to San100 (bottom) in steps of 20 mol%. The laser beam was focused on the cleavage plane (001) with the laser polarisation parallel to direction [010] (perpendicular to [100]). Bands A–D are indicated by dashed lines.

to estimate $K/(Na+K)$ for sanidine or anorthoclase, respectively. Band C turned out not to be suitable for a correlation with composition (see below).

For the evaluation of the Raman spectra, the raw spectra were baseline corrected by fitting a straight line between the relative minima at $\sim 230 \pm 10\text{ cm}^{-1}$ and $\sim 690 \pm 10\text{ cm}^{-1}$. We are aware that such simplified baseline may not correspond to the true spectral background, but it represents a simple way of data reduction that could consistently be applied with good reproducibility to all spectra. To determine peak positions, two different approaches were used. The first method was to fit the entire spectral region of interest with a minimum number of mixed Gaussian-Lorentzian bands. The low frequency region of band A (100 – 230 cm^{-1}) was fitted with 5 or 6 bands, for the frequency region of bands B–D (420 – 560 cm^{-1}) three bands were used. All fits were performed using the LabSpec 5 software of Horiba Jobin Yvon, applying the following protocol: (1) Cutting the spectral region of interest from the baseline subtracted spectrum. (2) Manually adjusting mixed Gaussian-Lorentzian bands to the relative maxima or shoulders. (3) Fitting the spectrum without further constraints on peak positions, line width or line shape. An example of such fits is shown in Fig. 2.

As an alternative to the time-consuming spectral fitting, we applied a second, much simpler approach to determine the positions of bands A and D, by manually adjusting a single Gaussian-Lorentzian band to the peak of interest (Fig. 3). This procedure may not reflect the true line shape and intensity of the Raman band, but will yield maximum positions with good reproducibility. As long as overlap with neighbouring bands is small, the obtained positions will only slightly deviate from the true values.

In order to test how crystal orientation affects the determination of peak maximum positions, we collected Raman spectra of several alkali feldspars (San0, San50, San100) as a function of the crystal orientation with respect to the laser polarisation (laser focused on the cleavage plane (001)). These measurements show that (1) a reliable evaluation of bands A and B is only possible for a limited range of angles of about ± 30 – 45° relative to [010]; at higher angles the peak intensities become too weak (position of band B can reliably be determined only for sanidine); (2) in this angular range each evaluation method yields nearly constant positions for band A (standard deviation $< 0.4\text{ cm}^{-1}$), (3) the intensities of bands C and D are only moderately orientation dependent, with little variation in position (standard deviations of less than 0.5 and 0.1 cm^{-1} for bands C and D, respectively).

4. Results and discussion

The positions of the Raman bands A to D of the synthetic sanidine – analbite series are listed in Table 1. Both evaluation methods, *i.e.* complete fitting of the spectral region of interest with several bands or manually adjusting a single band to the peak of interest, yield similar results for bands A and D (Table 1). The Raman shift of band A

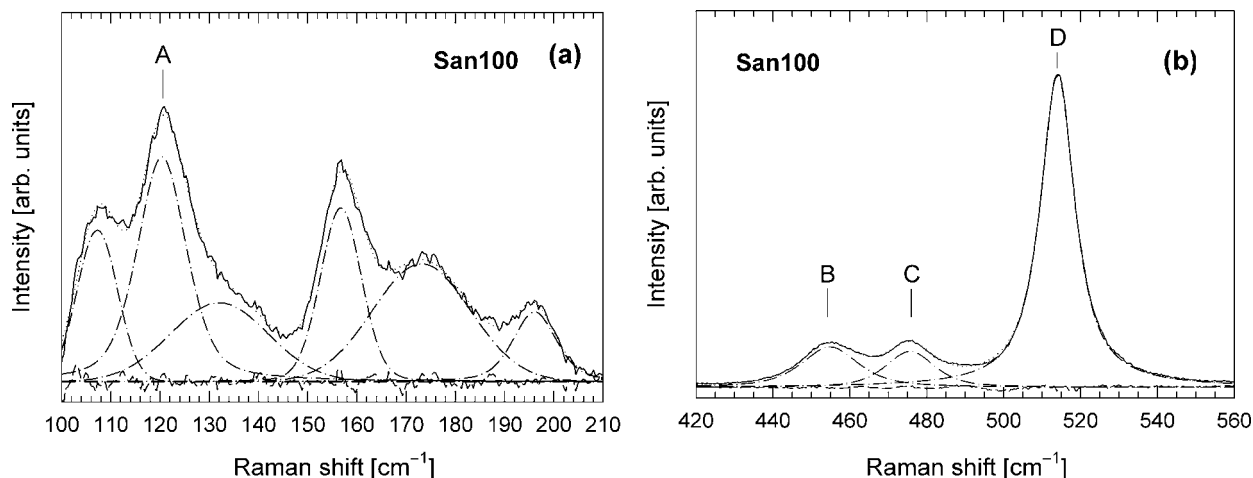


Fig. 2. Determination of the positions of (a) band A and (b) bands B–D by fitting the spectral region of interest with mixed Gaussian-Lorentzian bands.

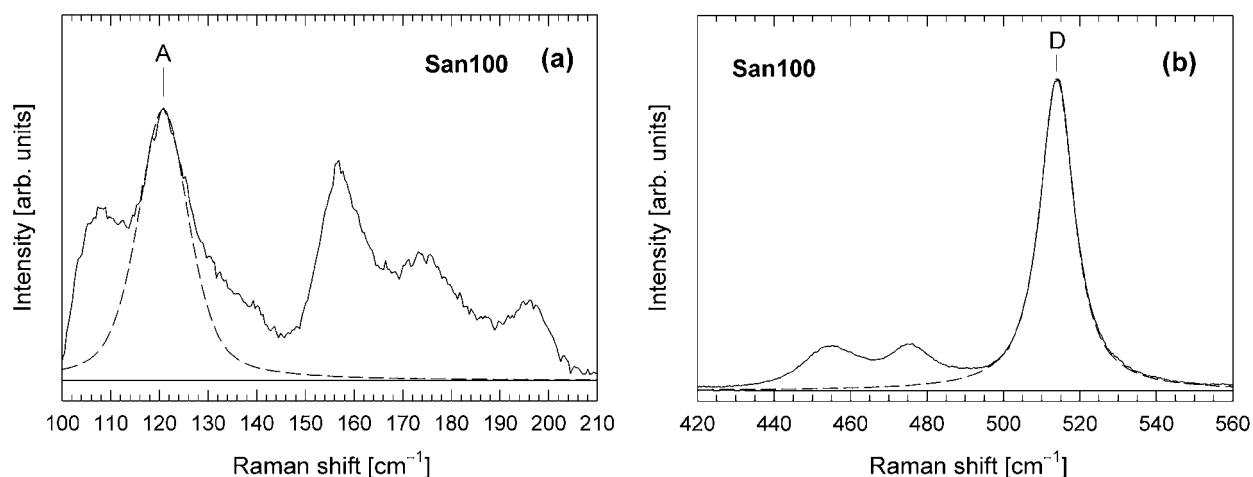


Fig. 3. Determination of peak positions by manually adjusting mixed Gaussian-Lorentzian bands to (a) band A and (b) band D.

varies between 120 cm^{-1} for pure sanidine and 142 cm^{-1} for pure analbite (Fig. 4). The correlation between Raman shift and chemical composition ($K/(Na+K)$) follows two linear trends with an intersection at about $K/(Na+K) = 0.32$, which is probably due to the phase transition between triclinic and monoclinic crystal structure, thus separating sanidine ($K/(Na+K) \approx 0.32 - 1$, space group $C2/m$) from anorthoclase ($K/(Na+K) \approx 0 - 0.32$, space group $C\bar{1}$). According to Kroll *et al.* (1986) and Zhang *et al.* (1996) this phase transition occurs on the binary join sanidine – analbite between 34 and 37 mol% sanidine. In the Raman spectra the transition from monoclinic sanidine to triclinic anorthoclase is visualised by the appearance of a new band at about 575 cm^{-1} (Fig. 1). By applying two linear regressions to the data of the synthetic series (positions obtained from peak fitting), the following correlations were obtained:

Anorthoclase:

$$K/(Na + K) = 4.5077 (0.2516) - 0.0316 (0.0018) \cdot RS \quad (1a)$$

$$(\sigma_{\text{est}} = 0.0181, R^2 = 0.9873)$$

Sanidine:

$$K/(Na + K) = 7.6375 (0.2791) - 0.0550 (0.0022) \cdot RS \quad (1b)$$

$$(\sigma_{\text{est}} = 0.0204, R^2 = 0.9920),$$

with RS being the Si corrected Raman shift of band A in cm^{-1} . Numbers in parentheses are the standard errors of the

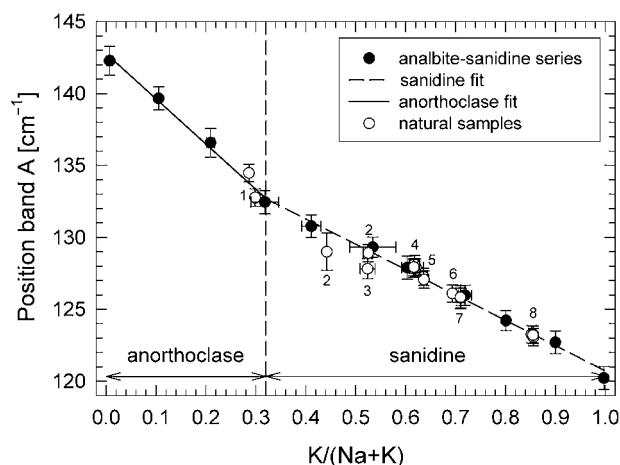


Fig. 4. Calibration curves for band A as a function of $K/(Na+K)$. The error in composition for most samples is smaller than the symbol size. The error in Raman shift was obtained by error propagation from the standard deviations of the peak position measurements and the wavenumber precision (0.3 cm^{-1}) and accuracy (0.5 cm^{-1}) of the Raman spectrometer. Separate linear regressions for synthetic anorthoclase ($K/(Na+K) < 0.32$) and sanidine ($K/(Na+K) > 0.32$) yield the correlations given in equation (1). Peak positions for the natural samples are labelled 1: BHH; 2: PRR; 3: TDF crystal 2; 4: SCE; 5: TDF crystal 1 + 3; 6: RG; 7: MPR; 8: SVF.

coefficients, σ_{est} is the standard error of the estimate for $K/(Na+K)$ and R^2 is the coefficient of determination. Using these correlations, the molar percentage of sanidine (defined here as $[\text{sanidine}]/([\text{sanidine} + \text{analbite}]) \times 100$, by neglecting anorthite, celsian and Sr-feldspar components) in the synthetic feldspar series can be determined with an accuracy of about 4 mol% ($2\sigma_{\text{est}}$) for both, anorthoclase and sanidine. When the calibration is applied to samples with unknown $K/(Na+K)$, it must be decided which correlation has to be used (equations (1a) or (1b)). Here, the distinguishing factor is a Raman shift of 132.5 cm^{-1} for band A. For values below 132.5 cm^{-1} equation 1a has to be applied, and for values above that number equation (1b) must be used. In the range 130 to 135 cm^{-1} , the application of the wrong correlation would induce an error of less than 8 mol% sanidine component.

In order to test the applicability of this calibration to natural samples, we obtained Raman spectra of several natural disordered alkali feldspars ranging in $K/(Na+K)$ from 0.286 to 0.856. Unfortunately, only one natural anorthoclase sample (BHH) was available, with a $K/(Na+K)$ ratio of about 0.29 ± 0.01 (Table 2). The data of the natural samples plot close to the calibration lines of the synthetic feldspars with only small deviations (Fig. 4), indicating that these calibrations can be used to estimate the Na/K ratio in natural samples (the maximum uncertainties are less than 10 mol% sanidine). Although some natural samples have larger amounts of Ca and Sr, but less Ba than the synthetic feldspar series (e.g. SCE: $\sim 0.9 \text{ wt\%}$

CaO, $\sim 0.2 \text{ wt\%}$ BaO; BHH: $\sim 2 \text{ wt\%}$ CaO, $\sim 0.8 \text{ wt\%}$ SrO, $\sim 0.2 \text{ wt\%}$ BaO, corresponding to up to $\sim 9.4 \text{ mol\%}$ anorthite and $\sim 2.2 \text{ mol\%}$ Sr-feldspar components), there are no significant deviations from the synthetic feldspar calibration, indicating that the position of band A is not highly influenced by the small amounts of Ca, Ba and Sr that are usually contained in alkali feldspars.

The Raman bands C and D are less orientation dependent and have high intensities in all directions. For the synthetic samples, the Raman shift of band C shows two opposite trends with chemical composition (Table 1): in the range $K/(Na+K) = 0.0 - 0.3$ the position decreases with increasing $K/(Na+K)$ and in the range $K/(Na+K) = 0.5 - 1.0$ the position increases. In between there is a broad minimum. Therefore the variation of band C with composition does not allow an estimation of the $K/(Na+K)$ ratio of disordered alkali feldspars. Furthermore, some natural feldspars with intermediate composition show a strong deviation from the trend of the synthetic series (Table 2). The reason for these deviations is not clear, as there is no obvious correlation with the fractions of anorthite, celsian and Sr-feldspar (samples PRR, BHH and TDF crystal 2, which show large offsets from the synthetic series, range between 0.6–9.4 mol% in An, 0–1.0 mol% in Cn and 0–2.2 mol% in Sr-Fsp components, Table 2). Another possibility is that these feldspars may have a different degree of Al-Si order compared to the fully disordered samples of the synthetic series, which may lead to additional peak shift. However, further investigations would be necessary to test this hypothesis.

Band D shows a clear variation of Raman shift with chemical composition only for anorthoclase ($K/(Na+K) \leq 0.32$), where the position varies from about 510 to 514 cm^{-1} (Fig. 5). In this range, the correlation is approximately linear with a positive slope with increasing $K/(Na+K)$. For sanidine ($K/(Na+K) > 0.32$), the position of band D remains constant at $514 \pm 0.5 \text{ cm}^{-1}$. Our natural alkali feldspars show only small deviations from the trend of the synthetic samples, indicating that also band D is not significantly influenced by small amounts of An, Cn and Sr-Fsp components. However, this band may only be suitable for the quantification of anorthoclase, but its applicability should be tested with more natural samples with $K/(Na+K) = 0.0 - 0.28$, which were not available for this study.

For sanidine, the chemical composition maybe estimated from the Raman shifts of band B. As shown in Fig. 1, band B is clearly separated from C for K-rich sanidine (100–70 mol% San component), but merges with band C for more Na-rich samples. In the range 60–30 mol% San, band B appears still as a shoulder at the low-wavenumber side of band C. Therefore the position of B can only be determined by peak fitting. In the spectra of anorthoclase the shoulder even disappears, leading to an asymmetric envelope of B and C. Therefore, the fits for anorthoclase are much less constrained than for sanidine, resulting in a much higher uncertainty in peak position of B (Table 1). For this reason we conclude that band B may

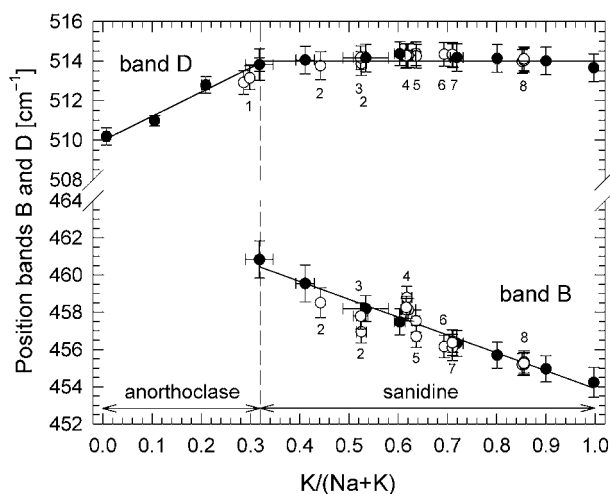


Fig. 5. Calibration curves for band B and D as a function of $K/(Na+K)$. The error in composition for most samples is smaller than the symbol size. The error in Raman shift was obtained by error propagation from the standard deviations of the peak position measurements and the wavenumber precision (0.3 cm^{-1}) and accuracy (0.5 cm^{-1}) of the Raman spectrometer. The peak positions of the natural samples are labelled 1: BHH; 2: PRR; 3: TDF crystal 2; 4: SCE; 5: TDF crystal 1 + 3; 6: RG; 7: MPR; 8: SVF.

only be used for the estimation of the $K/(Na+K)$ ratio in sanidine. For the synthetic samples, band B varies linearly from $\sim 461 \text{ cm}^{-1}$ for San30 to $\sim 454 \text{ cm}^{-1}$ for San100 (Fig. 5, Table 1). The natural sanidine follow the same trend, but deviate by up to 17 mol% San component from the correlation for the synthetic samples. Thus, the calibration of band B is less suitable for the application to unknown natural samples compared to the calibration of band A. However, it may still be useful for providing at least a rough estimate of composition in cases where band A cannot be observed.

An alternative to the calibration of band A (Fig. 4, equation (1)), is to use the difference between the positions of bands D and A ($\Delta DA = \text{Raman shift band D} - \text{Raman shift band A}$, Fig. 6). The main advantage of using ΔDA is that it does not require a careful correction of the Raman spectra with a standard and that the uncertainty due to the error in absolute wavenumber accuracy of the spectrometer cancels out. Furthermore, the changes in Raman shift add together as the peak positions show opposite trends with composition (at least for the anorthoclase, Figs. 4 and 5). Linear regressions to the data of the synthetic series (positions obtained from peak fitting) yield the correlations:

Anorthoclase:

$$K/(Na + K) = -8.3608 (0.4074) + 0.0228 (0.0011) \Delta \cdot DA \quad (2a)$$

$$(\sigma_{\text{est}} = 0.0111, R^2 = 0.9955),$$

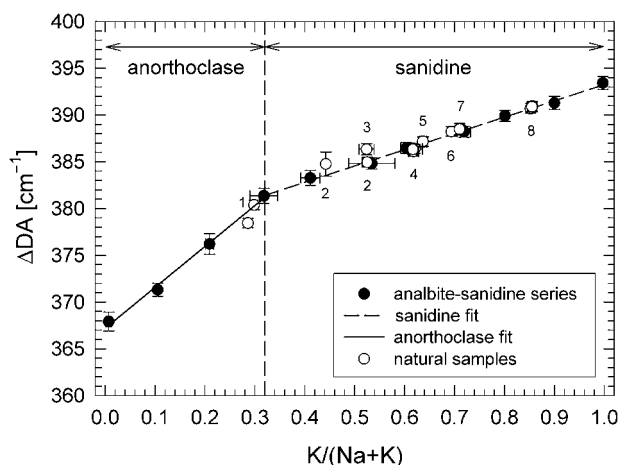


Fig. 6. Calibration curves of the difference between bands D and A (ΔDA) as a function of $K/(Na+K)$. The error in composition for most samples is smaller than the symbol size. The error in Raman shift was obtained by error propagation from the standard deviations of the peak position measurements and the wavenumber precision (0.3 cm^{-1}) of the Raman spectrometer. Separate linear regressions for synthetic anorthoclase ($K/(Na+K) < 0.32$) and sanidine ($K/(Na+K) > 0.32$) yield the correlations given in equation (2). The peak positions of the natural samples are labelled 1: BHH; 2: PRR; 3: TDF crystal 2; 4: SCE; 5: TDF crystal 1 + 3; 6: RG; 7: MPR; 8: SVF.

Sanidine:

$$K/(Na + K) = -21.5327 (0.6459) + 0.0573 (0.0017) \Delta \cdot DA \quad (2b)$$

$$(\sigma_{\text{est}} = 0.0147, R^2 = 0.9958),$$

with ΔDA in cm^{-1} . Numbers in parentheses are the standard errors of the coefficients, σ_{est} is the standard error of the estimate for $K/(Na+K)$ and R^2 is the coefficient of determination. The natural samples follow closely the trends of the synthetic series with maximal deviations of 7 mol% San component (for the average values), suggesting that ΔDA is best suited for the determination of $K/(Na+K)$ ratios in disordered alkali feldspars. It should also be noted that the manual peak adjustment gave very similar results for ΔDA (Tables 1 and 2), indicating that complete fitting of the relevant spectral regions has no significant advantage for the determination of the positions of bands A and D.

The good agreement of the data for the natural samples with the regressions obtained for the synthetic series suggests that the correlations presented in equation (1) and (2) can be used to estimate the Na/K ratio in “normal” natural disordered alkali feldspars, at least for sanidine. Due to the lack of natural anorthoclase with $K/(Na+K) < 0.28$ available in this study, the application of equations (1a) and (2a) to unknown natural samples requires further testing.

It should also be noted here that the data of Mernagh (1991) and preliminary data obtained in our laboratory

indicate that disordered alkali feldspars can be distinguished by Raman spectroscopy from ordered alkali feldspars and plagioclases. The spectral differences between ordered and disordered alkali feldspars are quite obvious as the Raman bands of the ordered series microcline – albite are much narrower and more numerous. For example in the range $240\text{--}300\text{ cm}^{-1}$ only one broad and asymmetric peak is observed for the sanidine – analbite series, which splits into three well resolved bands in the ordered series. A similar behaviour is observed in the range $700\text{--}830\text{ cm}^{-1}$ where ordered alkali feldspars display two narrow bands that are separated by more than 50 cm^{-1} (instead of one broad peak due to strongly overlapping bands for the disordered series). Similar narrow bands are observed for well ordered Na-rich plagioclase (albite, peristerite). However, the Raman spectra of plagioclase with intermediate structure ($\text{Ab}_{78}\text{An}_{22}\text{--}\text{Ab}_{27}\text{An}_{73}$) show a general resemblance to those of disordered alkali feldspars. Nonetheless, sanidine can readily be discriminated from plagioclase as the latter contains a band between 555 and 575 cm^{-1} , which in sanidine is absent (Fig. 1; Mernagh, 1991). However, this band is present in anorthoclase (at about 575 cm^{-1}), but in plagioclase it shifts towards lower wavenumbers with increasing An-component (e.g. to $570\text{--}560\text{ cm}^{-1}$ for intermediate plagioclase and 555 cm^{-1} for anorthite, Mernagh, 1991), thus enabling a distinction. Further discrimination between the different feldspar groups may be possible by comparison of bands occurring in the $T\text{--}O$ stretching region $900\text{--}1200\text{ cm}^{-1}$ (Mernagh, 1991).

The Raman calibrations presented here are not meant to replace EMP analysis, but can be used as a fast compositional check of natural and synthetic alkali feldspars with small preparative effort. A particular application is the analysis of samples with high value or small sample volume, for which embedding in epoxy resin and polishing should be avoided. Another useful application is the analysis of microlites in volcanic rocks, which are difficult to be analysed by other micro-beam techniques such as EMP. In case of (sub) micrometer-sized crystals, EMP would yield a mixed analysis of the crystal and the surrounding matrix (e.g. glass). Although the spatial resolution of modern micro-Raman spectrometers ($1\text{ }\mu\text{m}$ lateral, $3\text{--}5\text{ }\mu\text{m}$ in depth) is similar to that of an electron microprobe, and some of the Raman signal may also originate from the surrounding matrix, the feldspar peak positions will not be influenced, thus yielding accurate analyses. Furthermore, Raman calibrations like the one presented here, may be useful for the evaluation of Raman spectra obtained in future space missions (e.g. ExoMars Pasteur Mars landing mission of the European Space Agency), which will be equipped with Raman spectrometers.

5. Conclusions

This study demonstrates that Raman spectroscopy can be used to estimate the Na/K ratio of disordered alkali feldspars. The calibration presented here for the Raman band

between 120 and 142 cm^{-1} (band A) is insignificantly influenced by small amounts of other feldspar components (An, Cn, Sr-Fsp) and yields K/(Na+K) ratios with an accuracy of better than 0.1 , considering a number of different natural samples. By using the Raman shift difference between the most intense Raman band ($510\text{--}514\text{ cm}^{-1}$, band D) and band A (ΔDA) the accuracy can even be improved. However, to achieve the highest possible accuracy and to minimise possible effects due to different Raman equipment, future users may be required to produce their own calibration curves, or should at least verify the correlations presented here with few samples of known composition. Furthermore, the accuracy of the correlations for anorthoclase needs to be further constrained with the help of more natural samples. Also for more “exotic” alkali feldspars containing large amounts of Fe, Ba and Sr, the application of equations (1) and (2) may lead to higher uncertainties than for “normal” alkali feldspars containing only minor amounts of these elements. It is also desirable that future Raman calibrations will be performed for the plagioclase solid solution and for the effect of order-disorder phenomena in alkali feldspars.

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