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Raman spectroscopic characterisation of disordered alkali feldspars along the join $KAlSi_3O_8$–$NaAlSi_3O_8$: 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–analbite 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 K/(Na+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 (K/(Na+K) $<$ 0.32) the Raman shift (RS) of band A is related to composition by K/(Na+K) = 4.5077 − 0.0316 · RS. For sanidine (K/(Na+K) $>$ 0.32) the correlation K/(Na+K) = 7.3675 − 0.0550 · RS was obtained. Both correlations allow the determination of K/(Na+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 (K/(Na+K) = 0.28 − 0.86) from various volcanic rocks. These data suggest that the calibration can be used to estimate the K/(Na+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 K/(Na+K) = −8.3608 + 0.0228 · ΔDA and K/(Na+K) = −21.5327 + 0.0573 · ΔDA were obtained for anorthoclase and sanidine, respectively. These correlations allow the determination of K/(Na+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 ($NaAlSi_3O_8$–$KAlSi_3O_8$) 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 ($NaAlSi_3O_8$) 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*.,

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