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Calibration of a QEM-EDS system for rapid determination of potassium concentrations of feldspar grains used in optical dating

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Abstract

© 2020 Elsevier B.V. Potassium (K)-rich feldspars are one of two mineral types typically used for optical dating. Feldspar grains can contain up to ~14 wt% K that gives rise to an internal dose rate component. This internal component can comprise a significant proportion of the total environmental dose rate to which a mineral grain is exposed. The environmental dose rate term—the denominator in the optical age equation—determines the rate at which electronic charge is transferred into the crystal lattice of a mineral grain over its period of burial. Not all feldspar grains have the same K concentration, so internal dose rates differ between individual grains. K concentrations can range from 0 to 14 wt% due to the variable compositions of feldspar phases, differing proportions of discrete feldspar phases and/or the presence of other mineral inclusions in grains. Numerous techniques are available for determining the K concentrations of individual grains, but are time-consuming, and either lack the spatial resolution to classify discrete mineral phases within multi-phase grains, or the coverage to obtain whole-of-grain average K concentrations. Quantitative evaluation of minerals using energy dispersive spectroscopy (QEM-EDS) is a time-efficient and automated mapping technique that has the spatial resolution to classify most mineral phases, as well as the coverage to determine their area proportions. QEM-EDS can also be used to determine elemental concentrations based on spectral matches to EDS reference spectra. It is, however, difficult to determine accurate elemental concentrations for minerals such as feldspars, where solid solutions exist. To overcome this, we establish a QEM-EDS calibration using EDS spectra from six feldspar reference standards to define five solid solution regions along the alkali and plagioclase feldspar series. We test this calibration through comparisons of the K concentrations of discrete phases of three feldspar varieties (orthoclase/microcline, albite and sanidine), derived using both QEM-EDS and wavelength dispersive spectroscopy (WDS). We assume that the WDS-derived K concentrations represent the 'true' K concentrations of the phases, and calculate, from a best-fit weighted regression of the two data sets, a correction and uncertainty estimate that can be applied to the QEM-EDS-derived K concentrations, taking into account instrument irreproducibility and any measurement bias. We also test alternative mapping step sizes to optimise efficiency, and apply this time-efficient technique to individual luminescent feldspar grains from two samples. We propose that QEM-EDS is capable of (1) classifying the range of mineral phases in grains, (2) determining the area proportions of each of these phases, and (3) obtaining accurate whole-of-grain average K concentrations of individual feldspar grains using the calibration and correction presented here.

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Calibration of a QEM-EDS system for rapid determination of potassium concentrations of feldspar grains used in optical dating

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Abstract

Potassium (K)-rich feldspars are one of two mineral types typically used for optical dating. Feldspar grains can contain up to ~14 wt% K that gives rise to an internal dose rate component. This internal component can comprise a significant proportion of the total environmental dose rate to which a mineral grain is exposed. The environmental dose rate term—the denominator in the optical age equation—determines the rate at which electronic charge is transferred into the crystal lattice of a mineral grain over its period of burial. Not all feldspar grains have the same K concentration, so internal dose rates differ between individual grains. K concentrations can range from 0 to 14 wt% due to the variable compositions of feldspar phases, differing proportions of discrete feldspar phases and/or the presence of other mineral inclusions in grains. Numerous techniques are available for determining

the K concentrations of individual grains, but are time-consuming, and either lack the the spatial resolution to classify discrete mineral phases within multi-phase grains, or the coverage to obtain whole-of-grain average K concentrations. Quantitative evaluation of minerals using energy dispersive spectroscopy (QEM-EDS) is a time-efficient and automated mapping technique that has the spatial resolution to classify most mineral phases, as well as the coverage to determine their area proportions. QEM-EDS can also be used to determine elemental concentrations based on spectral matches to EDS reference spectra. It is, however, difficult to determine accurate elemental concentrations for minerals such as feldspars, where solid solutions exist. To overcome this, we establish a QEM-EDS calibration using EDS spectra from six feldspar reference standards to define five solid solution regions along the alkali and plagioclase feldspar series. We test this calibration through comparisons of the K concentrations of discrete phases of three feldspar varieties (orthoclase/microcline, albite and sanidine), derived using both QEM-EDS and wavelength dispersive spectroscopy (WDS). We assume that the WDS-derived K concentrations represent the ‘true’ K concentrations of the phases, and calculate, from a best-fit weighted regression of the two data sets, a correction and uncertainty estimate that can be applied to the QEM-EDS-derived K concentrations, taking into account instrument irreproducibility and any measurement bias. We also test alternative mapping step sizes to optimise efficiency, and apply this time-efficient technique to individual luminescent feldspar grains from two samples. We propose that QEM-EDS is capable of (1) classifying the range of mineral phases in grains, (2) determining the area proportions of each of these phases, and (3) obtaining accurate whole-of-grain average K concentrations of individual feldspar grains using the calibration and correction presented here.

1. Introduction

The development of post-infrared infrared stimulated luminescence (pIRIR) procedures (Thomsen et al., 2008; Buylaert et al., 2009; Li and Li, 2011) has improved the reliability of the use of potassium (K)-rich feldspar grains for optical dating of sediments. Measurement of the pIRIR signals can circumvent (or, at least, reduce) the effect of anomalous fading (Wintle, 1973), and overcome age underestimation. One advantage of using K-rich feldspar is its large internal dose rate contribution from the radioactive decay of ^{40}K , which is unaffected by changes in sediment moisture content and heterogeneity in the external beta dose rate (Godfrey-Smith et al., 2005; Li et al., 2014). One complication to this is that feldspar grains can have K concentrations ranging from 0 to 14 wt%. Internal dose rates may, therefore, differ between individual grains. For measurements of individual feldspar grains in optical dating, it is important to investigate the distributions of both equivalent dose (D_e) values and K concentrations among the sample of luminescent grains.

Feldspars are divided into two solid solution series: the alkali and plagioclase feldspar series. The alkali feldspar series has two common endmembers, Or (KAlSi_3O_8) and Ab ($\text{NaAlSi}_3\text{O}_8$), containing ~14 and 0 wt% K, respectively (Fig. 1). Depending on the geological source, two types of textures are found in sedimentary feldspars: single- and two-phase crystals. In volcanic terranes, rapidly quenched magmas produce high temperature, single-phase alkali feldspar crystals (sanidine, anorthoclase and albite; Fig. 1a), with varying concentrations of K and Na. These crystals may form overgrowths during diagenesis, however, resulting in two-phase alkali feldspar crystals. In plutonic terranes, where the magmas have cooled slowly, alkali feldspars almost always occur as low temperature, two-phase crystals. This is due to the unmixing of alkali feldspars into two minerals: one rich in K (orthoclase or microcline) and the other rich in Na (albite) (Fig. 1b). This unmixing results in intergrowths of the two feldspar phases, referred to as perthitic textures.

Figure 1: Ternary diagram of feldspars (modified from Parsons, 2010), showing possible compositions of feldspars in the alkali and plagioclase feldspar series occurring between the Or (KAlSi_3O_8), Ab ($\text{NaAlSi}_3\text{O}_8$) and An ($\text{CaAl}_2\text{Si}_2\text{O}_8$) endmembers at (a) high temperature and (b) low temperature. K-rich (>9.4 wt% K) feldspar is shown in the blue shaded regions, and low-K (<9.4 wt% K) feldspar is shown in the pink shaded regions. The unshaded regions indicate feldspar compositions that do not occur in nature.

In optical dating, K-rich feldspar grains are usually targeted for infrared stimulated luminescence (IRSL) and pIRIR measurements. These grains are separated from sieved sediment samples using a heavy liquid such as sodium polytungstate diluted to a density of 2.58 g.cm^{-3} (Wintle, 1997). In theory, this will preferentially float off single- and two-phase alkali feldspar grains with K concentrations of >9.4 wt% (blue shaded regions in Fig. 1), assuming densities of 2.56 and 2.62 g.cm^{-3} for the Or and Ab endmembers. As a result, grains from the ‘K-rich’ (< 2.58 g.cm^{-3}) feldspar fraction are often assumed to have, on average, K concentrations of $12.5 \pm 0.5 \text{ wt\%}$ (Huntley and Baril, 1997). Density separations are, however, imperfect. Some studies have shown that ‘K-rich’ feldspar fractions can also contain low-K (<9.4 wt% K) feldspar grains (pink shaded regions in Fig. 1), as well as other minerals that may occur as inclusions in feldspar grains (e.g., Dütsch and Krbetschek, 1997; Huntley and Baril, 1997; Godfrey-Smith et al., 2005), resulting in individual luminescent feldspar grains with K concentrations ranging from 0 to 14 wt% (e.g., Willerslev et al., 2007; Feathers, 2012; Huot and Lamothe, 2012; Neudorf et al., 2012; Smedley et al., 2012, 2016; Gaar et al., 2014; Trauerstein et al., 2014; Sutikna et al., 2016; Buylaert et al., 2018; Jacobs et al., 2019; Rui et al., 2019). This has

implications for estimating D_e values for grains individually, and determining optical ages using average K concentrations for internal dose rate calculations.

It is important to consider the entire grain, not only the luminescent feldspar phase, when determining internal dose rates. Determining K concentrations of single-phase feldspar grains is analytically straightforward, but obtaining whole-of-grain average K concentrations for multi-phase grains is challenging. Several different techniques have been used to determine K concentrations for individual luminescent feldspar grains. These include laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; e.g., Willerslev et al., 2007; Smedley et al., 2012, 2016), micro X-ray fluorescence (μ XRF; e.g., Buylaert et al., 2018), energy dispersive spectroscopy (EDS; e.g., Willerslev et al., 2007; Feathers, 2012; Huot and Lamothe, 2012; Sutikna et al., 2016; Rui et al., 2019) and wavelength dispersive spectroscopy (WDS; e.g., Huot and Lamothe, 2012; Neudorf et al., 2012; Gaar et al., 2014; Trauerstein et al., 2014; Sutikna et al., 2016; Jacobs et al., 2019). Each of these techniques have their advantages and limitations.

All four techniques can determine K concentrations of discrete feldspar phases accurately, if measurements are performed correctly. LA-ICP-MS and μ XRF can measure a large volume proportion of a grain in a single analysis point, and can, therefore, incorporate representative proportions of both feldspar phases in a two-phase alkali feldspar grain to obtain whole-of-grain average K concentrations. EDS and WDS can only measure small area proportions of a grain in a single analysis point because flat surfaces are required, and for most natural feldspar grains, cracks and rough surface areas exist. LA-ICP-MS and μ XRF lack the spatial resolution to classify other mineral inclusions in feldspar grains; if other mineral inclusions are included in single analysis points, the whole-of-grain average K concentrations may be unreliable. EDS and WDS, alternatively, have the spatial resolution to classify most mineral phases; used in conjunction with backscattered electron (BSE) imaging, EDS and WDS are good at classifying mineral phases, and observing their distributions within grains. All four techniques require manual user input of a selection of single analysis points, each taking up to several

minutes. Each of these approaches can, therefore, be very time-consuming, and result in a limited number of measurements that can realistically be made. Although across these four techniques, most necessary information can be acquired, there is no single automated technique that can (1) reliably classify the range of mineral phases present in grains, (2) determine the area proportions of each of these phases, and (3) obtain accurate whole-of-grain average K concentrations.

Quantitative evaluation of minerals using energy dispersive spectroscopy (QEM-EDS) could potentially fill this role. QEM-EDS is a time-efficient and automated mapping technique that involves the use of a scanning electron microscope (SEM) equipped with multiple (2–4) EDS detectors (Sutherland et al., 1988; Sutherland and Gottlieb, 1991). An electron beam is scanned in a raster using discrete steps; EDS spectra are collected and stored for each point (or pixel) visited. The mineral phase at each pixel is classified by comparing the stored EDS spectrum to a library of reference spectra until a best spectral match is obtained. QEM-EDS has previously been used to classify and determine the area proportions of mineral phases within multi-phase grains used for optical dating (Meyer et al., 2013), but it can also be used to determine elemental concentrations. The latter generally works well for minerals with fixed compositions (such as quartz, SiO_2), but can be more problematic if solid solutions exist, as is the case for feldspars.

In this study, we describe our approach to refine a QEM-EDS calibration for feldspars, using EDS spectra from six feldspar reference standards to define five solid solution regions across the alkali and plagioclase feldspar series. Using this calibration, we classify discrete phases of three feldspar varieties (orthoclase/microcline, albite and sanidine) within natural feldspar grains, and derive K concentrations for these phases. We compare these QEM-EDS-derived K concentrations to WDS-derived K concentrations of the same phases, and assume that the latter represent the ‘true’ K concentrations. From a best-fit weighted regression of the two data sets, we calculate a correction, as well as an uncertainty estimate, that can be applied to the QEM-EDS-derived K concentrations of feldspar phases, taking into account instrumental irreproducibility and any measurement bias. We also test alternative

mapping step sizes for optimal measurement efficiency, and apply this measurement procedure to a large number of individual feldspar grains with detectable pIRIR signals extracted from two sediment samples collected from different geological provenances to investigate the distributions of K concentrations, as well as the possible relationship between pIRIR signal intensity and K concentration.

2. Samples and instruments

2.1. Sample details

Two sediment samples were used in this study: UK16-7, collected from Ust'-Karakol-1, an archaeological site in southern Siberia, and LBB15-6, collected from Leang Bulu Bettue, an archaeological site on the island of Sulawesi in Indonesia. Samples were treated with hydrochloric acid and hydrogen peroxide to remove carbonates and organic matter. Using grains of 180–212 μm in diameter, and sodium polytungstate solutions diluted to densities of 2.58 and 2.62 g.cm^{-3} , individual grains from two feldspar fractions—'K-rich' ($<2.58 \text{ g.cm}^{-3}$) and 'Na-rich' ($2.58\text{--}2.62 \text{ g.cm}^{-3}$)—were prepared for each sample for measurements of their pIRIR signals and K concentrations. Grains were not etched with hydrofluoric acid to avoid the deep etch pits that are known to occur in acid-etched feldspar grains (Duller, 1992; Porat et al., 2015); large proportions of cracks and rough surfaces are not ideal for WDS and QEM-EDS measurements. Subsequent to pIRIR measurements (Section 4.1), grains that passed rejection criteria were hand-picked from single-grain discs, mounted on a glass plate, and set in resin. Once cured, resin mounts were polished using 1 μm diamond paste to obtain a flat surface for grains, and coated with $\sim 25 \text{ nm}$ of carbon, for WDS and QEM-EDS measurements.

2.2. WDS

The compositions of feldspar phases within grains were assessed using the JEOL JXA-8530F Plus electron probe microanalyser housed in the Centre for Advanced Microscopy (CAM) at the Australian

National University (ANU), using an accelerating voltage of 15 kV, and a beam current of 20 nA. BSE imaging was used to observe the distributions of mineral phases, and WDS measurements were conducted on discrete feldspar phases using a beam diameter of 5 μm to minimise alkali loss during analysis. Astimex mineral standards of sanidine and albite were used as reference materials for WDS analyses. Feldspar phases were characterised by 3–7 point analyses per phase with totals of 99–101 wt%. Concentrations of Na_2O , MgO , Al_2O_3 , SiO_2 , Cl , K_2O , CaO , TiO_2 , MnO , FeO and BaO were obtained to account for the range of possible feldspar compositions, and to observe accidental inclusions of other minerals (or resin) in point analyses.

2.3. QEM-EDS

QEM-EDS maps of grains were obtained using the FEI Quanta QEMSCAN 650F housed in the CAM at ANU, using an accelerating voltage of 15 kV, which resulted in an interaction volume of 2–3 μm . The beam current was set at 10 nA, and the count rate was ~ 400 counts per ms. The total counts for each pixel was set at 6,000 counts, resulting in a dwell time of ~ 15 ms for each pixel. The smallest meaningful mapping step size of 2.5 μm (due to the size of the interaction volume) was used. This resulted in maps consisting of $\sim 5,000$ pixels for spherical grains of ~ 200 μm in diameter. The full spectrum QEM-EDS maps were processed using Nanomin[®] (ThermoScientific) software to correctly classify mineral phases at each pixel. Nanomin[®] uses a database of individual EDS reference spectra stored for each mineral composition, and searches for the best spectral match to establish a mineral classification.

3. Experimental details and results

3.1. Calibration of QEM-EDS for feldspars

There are a wide range of possible feldspar compositions that can occur throughout the alkali and plagioclase feldspar series, so natural feldspars of variable compositions may not have reliable matches

to individual EDS spectra of fixed composition reference feldspars. To track the variable compositions of natural feldspars, and obtain better spectral matches, it is possible to simulate solid solutions in Nanomin[®] using linear combinations of two or more reference spectra. The proportions of each reference spectrum required to obtain the best spectral match to EDS spectra of natural feldspars are obtained in this manner. The compositions of the reference feldspars are known, so the proportions of their spectra required to obtain the best spectral match can then be used to derive the compositions of natural feldspars.

The simplest approach to simulating solid solutions involves synthesising EDS reference spectra for the three common feldspar endmembers—Or, Ab and An ($\text{CaAl}_2\text{Si}_2\text{O}_8$)—and defining two solid solution regions (one each for the alkali and plagioclase feldspar series; Or–Ab and Ab–An) between pairs of these reference feldspars. Such uncalibrated QEM-EDS derived feldspar compositions are often unreliable, so we followed a three step approach to calibrate our QEM-EDS system for feldspars. First, we obtained EDS spectra from six well defined feldspar reference standards (Table 1), including in-house (orthoclase and anorthoclase), Astimex (sanidine, albite and labradorite), and Smithsonian (anorthite) reference standards. The compositions of the in-house reference standards were determined using WDS. Using real, rather than synthesised, EDS reference spectra, improved the quality of spectral fittings for natural feldspars because the spectra of natural and reference feldspars are measured in the same way, thus providing direct comparisons. Second, we defined five solid solution regions (shown as red arrows in Fig. 2) between pairs of these reference feldspars (shown as different coloured filled circles in Fig. 2). By defining five solid solution regions, rather than only two, we can better constrain the range of natural feldspar compositions, thus reducing systematic deviations from true elemental concentrations. Third, we used a minimum spectral fitting threshold of 95%, so pixels were only classified as feldspar (or other minerals) if their EDS spectra had matches to reference spectra (or linear combinations of reference spectra) with a goodness of fit >95%. This, along with the 6,000 counts obtained for each pixel, ensures the reliability of spectral matches.

Figure 2: Compositions of feldspar reference standards used to obtain reference spectra for the QEM-EDS calibration. Colours of filled circles indicate the colours assigned to each reference standard in Nanomin[®]. Red arrows indicate solid solution regions defined in Nanomin[®].

Each of the feldspar reference standards were assigned a different colour (Fig. 2); this is how pixels with spectral matches of 100% to each of the reference spectra are represented in the QEM-EDS maps. Pixels with spectral matches of 100% to the orthoclase, albite or anorthite reference spectra appear blue, green and yellow, respectively. The sanidine, anorthoclase and labradorite reference standards were assigned colours in proportion to their similarities in composition to the orthoclase, albite and anorthite reference standards. Pixels with spectral matches of 100% to the sanidine, anorthoclase and labradorite reference spectra, therefore, appear blue-green, green-blue and yellow-green, respectively. Pixels with spectral matches to a linear combination of two reference spectra have colours grading between the colours of the two constraining reference standards. Therefore, for alkali feldspars, colours grade between blue and green from orthoclase–sanidine, sanidine–anorthoclase, and anorthoclase–albite; for plagioclase feldspars, colours grade between green and yellow from albite–labradorite, and labradorite–anorthite.

3.2. Testing the accuracy of the QEM-EDS calibration for feldspars

3.2.1. Classifications and distributions of feldspar phases

To test the QEM-EDS calibration, we measured a number of discrete feldspar phases within grains from UK16-7 and LBB15-6 using both WDS and QEM-EDS. First, we obtained QEM-EDS maps to classify the feldspar phases, and observe their distributions in the grains. BSE images were also obtained prior to WDS measurements to guide the input of analysis points. Fig. 3 shows a selection of QEM-EDS maps (top) and BSE images (bottom) of grains from UK16-7 (Fig. 3a–c) and LBB15-6 (Fig. 3d–f). In general, grains from UK16-7 contain two alkali feldspar phases (orthoclase/microcline and albite), exhibiting fine (Fig. 3a) or coarse (Fig. 3b and c) perthitic textures. Most grains from LBB15-6 contain one alkali feldspar phase (sanidine; Fig. 3d and e), but some exhibit coarse perthitic textures similar to the grain from UK16-7 in Fig. 3b, or two feldspar phases with compositions characteristic of orthoclase/microcline and sanidine (Fig. 3f). The compositions of orthoclase/microcline and sanidine overlap (Fig. 1), however, so the ‘orthoclase/microcline’ classification is tenuous. The presence of orthoclase/microcline and sanidine in grains may be a result of diagenesis. In general, QEM-EDS mapping was capable of distinguishing between orthoclase/microcline, albite and sanidine, and other minerals, based on their compositions. BSE imaging could distinguish between mineral phases (with the notable exception of albite and quartz) based on relative differences in brightness and contrast of phases, which was sufficient for guiding the input of analysis points for WDS measurements.

Orthoclase	Albite	Quartz
Sanidine	Labradorite	Mica
Anorthoclase	Anorthite	Unclassified

Figure 3: QEM-EDS maps (top) and BSE images (bottom) of grains from (a–c) UK16-7 and (d–f) LBB15-6. The colours in the QEM-EDS maps correspond to mineral classifications, including feldspars, quartz and mica, as well as unclassified pixels. The colours of pixels classified as feldspar in the QEM-EDS maps may grade between those of the feldspar reference standards in the legend because solid solution regions were defined between pairs of these reference standards. The different greyscales in the BSE images correspond to the presence of elements with different atomic masses. Heavier elements cause more electrons to be ‘scattered’ and detected, resulting in brighter phases, while lighter elements ‘absorb’ more electrons, resulting in dimmer phases.

3.2.2. Comparisons of WDS- and QEM-EDS-derived K concentrations

Using the QEM-EDS maps and BSE images for guidance, we targeted a number of discrete orthoclase/microcline ($n = 11$) and albite ($n = 9$) phases within grains from UK16-7, and sanidine ($n = 12$) phases within grains from LBB15-6. We measured K (and other elemental) concentrations of these phases using WDS; their WDS-derived compositions are shown in ternary space in Fig. 4, with different symbols for the three feldspar varieties. We then compared the WDS- and QEM-EDS-derived K concentrations obtained for each of the feldspar phases (Fig. 5a). Mean K concentrations of multiple (3–7) point analyses per phase using WDS ranged from 13.4 to 13.9 wt% (orthoclase/microcline), 0.1 to 0.5 wt% (albite) and 8.7 to 13.1 wt% (sanidine). Single QEM-EDS area analyses of the same phases (using 5×5 pixel regions of interest) gave K concentrations ranging from 13.0 to 13.5 wt% (orthoclase/microcline), 0.3 to 0.8 wt% (albite) and 8.8 to 13.1 wt% (sanidine). As a way of illustrating the benefit of using our calibration approach (specifically the first two steps; Section 3.1), we show in Fig. 5b the same data as in Fig. 5a, but where we used synthesised EDS reference spectra for the three common feldspar endmembers—Or, Ab and An—to define only two solid solution regions: one each for the alkali and plagioclase feldspar series. This uncalibrated approach shows a systematic overestimation of the WDS-derived K concentrations of, on average, ~ 0.4 , ~ 0.4 and ~ 1.5 wt% for orthoclase/microcline, albite and sanidine phases, respectively; the improvement using our calibration is obvious.

Figure 4: WDS-derived compositions of orthoclase/microcline (open circles; $n = 11$) and albite (open triangles; $n = 9$) phases within grains from UK16-7, and sanidine (filled squares; $n = 12$) phases within grains from LBB15-6. The inset diagram shows the orthoclase/microcline phases that overlap with sanidine phases.

Figure 5: (a) QEM-EDS-derived K concentrations using the calibration established in this study, and (b) uncalibrated QEM-EDS-derived K concentrations, compared to WDS-derived K concentrations of feldspar phases within grains from UK16-7 and LBB15-6. The open circles, open triangles and filled squares represent orthoclase/microcline ($n = 11$), albite ($n = 9$) and sanidine ($n = 12$) phases, as in Fig. 4. The red stippled lines are 1:1 lines.

Fig. 6a–c shows the comparisons presented in Fig. 5a on reduced scales for the three feldspar varieties.

Using our QEM-EDS calibration, a systematic underestimation of WDS-derived K concentrations of ~ 0.3 wt% is present for orthoclase/microcline phases (Fig. 6a), and a systematic overestimation of ~ 0.5 wt% is present for albite phases (Fig. 6b). One albite and two orthoclase/microcline phases deviate

from these trends, and give consistent K concentrations using both techniques (shown as filled symbols in Fig. 6a and b). Their only apparent differences from other phases of the same variety are their higher WDS-derived Ba (orthoclase/microcline; ~ 0.3 and ~ 0.4 wt%) or Ca (albite; ~ 1.4 wt%) concentrations. The higher Ca concentration of this albite phase means that most pixels of this phase had best spectral matches to the albite–labradorite solid solution region, as opposed to the anorthoclase–albite solid solution region (Fig. 2), which is not the case for most pixels in other albite phases. The albite and labradorite reference standards have K concentrations of 0.18 and 0.34 wt% (Table 1), so the derived K concentrations of these pixels must occur between these two values. This resulted in a lower QEM-EDS-derived K concentration (which is closer to the WDS-derived K concentration) for this albite phase. The effect of the higher Ba concentrations of the two orthoclase/microcline phases on their QEM-EDS-derived K concentrations is less clear. No systematic differences between QEM-EDS- and WDS-derived K concentrations are observed for sanidine phases (Fig. 6c).

3.2.3. Instrumental reproducibility and measurement bias

We investigated two sources of potential uncertainty for the WDS- and QEM-EDS-derived K concentration comparisons: instrumental irreproducibility (random error) and measurement bias (systematic error). Instrumental irreproducibility was tested for both WDS and QEM-EDS. For WDS, multiple (3–7) point analyses were obtained for each feldspar phase, allowing for the calculation of standard errors, or random errors, of K concentrations for each feldspar phase. The standard errors are small, ranging from ± 0.01 to ± 0.23 wt% K. For QEM-EDS, instrumental irreproducibility was estimated from 15 area analyses (using 5×5 pixel regions of interest, the same as for the WDS- and QEM-EDS-derived K concentration comparisons) on one phase of each of the feldspar varieties (Fig. 6d). The calculated standard errors on these area analyses are ± 0.02 wt% K for orthoclase/microcline and sanidine, and ± 0.01 wt% K for albite. An estimate of measurement bias was determined from the pairwise differences between WDS- and QEM-EDS-derived K concentrations for each phase. The differences range from 0.00 to 0.69 wt% K, resulting in standard errors, or systematic errors, of ± 0.00

to ± 0.47 wt% K for orthoclase/microcline, ± 0.09 to ± 0.69 wt% K for albite, and ± 0.00 to ± 0.20 wt% K for sanidine. This systematic error is only applied to the QEM-EDS-derived K concentrations, and added in quadrature to the random error for each phase. The total standard errors for QEM-EDS-derived K concentrations range from ± 0.02 to ± 0.69 wt%.

Figure 6: (a–c) The same comparison curves as in Fig. 5a, but on reduced scales for (a) orthoclase/microcline (open circles; $n = 11$), (b) albite (open triangles; $n = 9$) and (c) sanidine (filled squares; $n = 12$), as in Figs 4 and 5. The filled symbols in (a) and (b) indicate feldspar phases that were identified as deviating from the trend. The red stippled lines are 1:1 lines. (d) QEM-EDS-derived K concentrations of one phase of each of the three feldspar varieties obtained from fifteen 5×5 pixel regions of interest.

3.2.4. A comparison curve and correction for QEM-EDS-derived K concentrations

We assumed that the WDS-derived K concentrations represent the ‘true’ K concentrations of each of the phases, and obtained a best-fit weighted regression line for the two data sets, using a Deming

function that takes into account the standard errors (Section 3.2.3) associated with both variables. If all phases were included, we obtained a line of best fit with a slope (m) of 0.9848 ± 0.0047 , a y-intercept (b) of 0.1681 ± 0.0544 , and a correlation coefficient of 0.9996. The three phases (two orthoclase/microcline and one albite) that show no bias and deviate from the main trends (Section 3.2.2) are more precise, and have a strong influence on the fit. These phases have slightly different elemental compositions, and do not represent the majority of phases. Thus, we excluded these three phases and obtained a line of best fit with $m = 0.9725 \pm 0.0068$, $b = 0.3005 \pm 0.0779$, and a correlation coefficient of 0.9997 (Fig. 7). The QEM-EDS-derived K concentrations of feldspar phases can now be projected onto this best-fit line and interpolated onto the x-axis to obtain ‘true’ (corrected) K concentrations. The 95.4% confidence interval (CI) of the regression line is shown in Fig. 7. For the orthoclase/microcline, albite and sanidine regions, the 95.4% CI ranges from ± 0.04 to ± 0.05 wt% K, ± 0.15 to ± 0.16 wt% K, and ± 0.03 to ± 0.05 wt% K, respectively. As a conservative estimate, we suggest using the upper range of around ± 0.2 wt% as a calibration uncertainty for all three feldspar varieties when determining K concentrations using the QEM-EDS calibration and correction described here.

Figure 7: Best-fit weighted regression line (red stippled line) fitted to QEM-EDS- and WDS-derived K concentrations of all feldspar phases shown in Figs 4–6, with the exception of three outliers (two orthoclase/microcline and one albite), assuming WDS-derived K concentrations represent the ‘true’ K concentrations. The two red solid lines represent the lower and upper boundaries of the 95.4% CI of the regression line. Error bars represent the standard errors on the WDS- and QEM-EDS-derived K concentrations at 2σ .

3.3. Calculating whole-of-grain average K concentrations

Now that we can classify, and derive accurate K concentrations of, discrete feldspar phases using QEM-EDS, we need to consider the entire grain. The QEM-EDS maps presented in Fig. 3a–c of grains from UK16-7 also show the presence of quartz (beige) and mica (red) that occur as inclusions. The mica phase was determined to occur in the celadonite ($\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})[\text{Si}_4\text{O}_{10}](\text{OH})_2$) to muscovite ($\text{KA}l_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$) solid solution series based on EDS measurements using the Hitachi 4300 SE/N Schottky field emission scanning electron microscope housed in the CAM at ANU. Quartz contains no significant amount of K, whereas K concentrations range from ~9.1 to ~9.8 wt% in the celadonite–muscovite solid solution series. This range of K concentrations, and the area proportions of these mica phases within grains from UK16-7 (~1%), are relatively small, so a specific QEM-EDS calibration and correction (as was done for feldspars) is not necessary. Instead, a solid solution region was defined between only two reference spectra (synthesised and real reference spectra for celadonite and muscovite, respectively), and the derived K concentrations are considered to be close to the true values. The uncalibrated QEM-EDS-derived K concentrations for feldspar phases shown in Fig. 5b deviate from the WDS-derived K concentrations by, at most, ~15% of the total range in K concentrations, ~14 wt%. If the same is true for the uncalibrated QEM-EDS-derived K concentrations of these mica phases, a maximum systematic deviation from true K concentrations of ~0.1 wt% can be expected.

The QEM-EDS maps presented in Fig. 3e and f (top) of grains from LBB15-6 show a number of unidentified (orange) mineral phases. At least two mineral phases could not be identified using EDS spectra due to their heterogeneity at a finer scale than the interaction volume of the QEM-EDS (2–3 μm), as can be seen in BSE images in Fig. 3e and f (bottom). These phases are likely to be clay minerals (e.g., kaolinite), and the result of chemical weathering of feldspars, but this could not be proven conclusively using either WDS or QEM-EDS. For LBB15-6, such unclassified phases are negligible

because they comprise, on average, only ~4% of grain areas. Since whole-of-grain average K concentrations are calculated from the derived K concentrations of each classified pixel, and assumed densities of minerals, however, the presence of too many unclassified pixels in a sample may be problematic. Depending on the compositions of the unclassified phases, and their area proportions and densities, too many unclassified pixels can result in significant systematic deviations from true whole-of-grain average K concentrations.

To calculate a whole-of-grain average K concentration for a grain, a region of interest is placed over the QEM-EDS map of this grain in Nanomin[®]. Each classified pixel in this region of interest has a K concentration and an assumed density. If a pixel, for example, has a spectral fitting of 50% to each of the orthoclase (~14 wt% K; 2.56 g.cm⁻³) and sanidine (~10 wt% K; 2.58 g.cm⁻³) reference spectra, it will have a derived K concentration of ~12 wt%, and an assumed density of 2.57 g.cm⁻³. The K concentrations of all classified pixels in a grain are weighted by their density; the whole-of-grain average K concentration is the mean of the density-corrected K concentrations of all classified pixels. This calculation is automatically achieved in Nanomin[®]. Table 2 shows the area proportions, densities and K concentrations of the classified phases of the six grains presented in Fig. 3, as well as their calculated whole-of-grain average K concentrations. For grains A, B and C (Fig. 3a–c), the area proportions of orthoclase/microcline were assumed to be equal to the sum of spectral fittings to the orthoclase and sanidine reference spectra, while the area proportions of albite were assumed to be equal to the sum of spectral fittings to the anorthoclase, albite and labradorite reference spectra. One problem with this approach of distinguishing between feldspar phases is that pixels may occur along the boundaries between orthoclase/microcline and albite phases, thus producing mixed EDS spectra of the two phases. This is particularly problematic for Grain A due its fine perthitic textures. In Table 2, this shows the K concentrations of orthoclase/microcline phases to be lower than their true values, and the K concentrations of albite phases to be higher than their true values. The same problem occurs to a lesser extent for grains B and C. This, however, has no impact on the reliability of whole-of-grain

average K concentrations because our calibration is suitable for the range of compositions between orthoclase/microcline and albite. For grains D, E and F, the area proportions of sanidine were assumed to be equal to the sum of spectral fittings to the orthoclase, sanidine and anorthoclase reference spectra. Since orthoclase/microcline is also defined by spectral fittings to the orthoclase and sanidine reference spectra, the possible ‘orthoclase/microcline’ and sanidine phases in Grain F could not be distinguished, and are presented together. Grains A, B, C and D contain <1% unclassified pixels, but grains E and F contain ~6.2% and ~4.8% unclassified pixels, which are not included in the calculation of whole-of-grain average K concentrations. The correction determined in Section 3.2.4 was applied to the combined feldspar phases within these grains, but made a negligible difference because most of these grains have derived K concentrations of combined feldspar phases in the range of 9.0–11.3 wt%, which is around the point where the best-fit weighted regression line crosses the 1:1 line. The correction is more important for grains containing combined feldspar phases with derived K concentrations closer to 0 or 14 wt%.

3.4. Optimising measurement procedures for routine analyses

For all of the above QEM-EDS measurements, we used a mapping step size of 2.5 μm , resulting in ~5,000 pixels in the map of a spherical grain of ~200 μm in diameter. Using the parameters described in Section 2.3, a dwell time of ~15 ms is required for each pixel, so it should take ~75 s to map such a grain. To take advantage of the automated system and maximise efficiency, it is best to run QEM-EDS maps overnight for close to 24 hrs. Using a 2.5 μm step size, it is feasible to measure ~600 grains in 24 hrs, including set-up time of ~2 hrs and time for the system to classify the embedding resin as background. Five thousand pixels may be more than is necessary to determine reliable area proportions of mineral phases within grains, so we tested, using 87 grains from UK16-7 and LBB15-6, the impact of using two alternative step sizes—5 μm and 10 μm —on the accuracy of whole-of-grain average K concentrations. This increased the possible number of grains measured in 24 hrs to ~2,400 and ~9,600, respectively, but reduced the number of pixels in the maps by four and 16 times. The differences

between the K concentrations obtained using a 5 μm compared to 2.5 μm step size are, on average, 0.04 wt%, with a maximum of 0.16 wt% (crosses in Fig. 8). Differences in K concentrations obtained using a 10 μm compared to a 2.5 μm step size are greater (mean = 0.07 wt% and maximum = 0.50 wt%; open diamonds in Fig. 8). Grains that show the greatest differences in K concentrations contain three or more mineral phases, similar to the grain presented in Fig. 3c, so the differences in K concentrations can be attributed to the lower resolution of the larger mapping step size obtaining less reliable area proportions of mineral phases. The use of a 5 μm step size appears to be a good compromise between time-efficiency and accuracy of whole-of-grain average K concentrations.

Figure 8: Differences in QEM-EDS-derived whole-of-grain average K concentrations of 87 grains measured using mapping step sizes of 5 μm (crosses) and 10 μm (open diamonds) from those measured using a step size of 2.5 μm .

4. Application and discussion

4.1. Grain selection and pIRIR measurements

Prior to the measurements described above, individual grains from the ‘K-rich’ ($<2.58 \text{ g.cm}^{-3}$) and ‘Na-rich’ ($2.58\text{--}2.62 \text{ g.cm}^{-3}$) feldspar fractions of UK16-7 and LBB15-6 were loaded onto standard aluminium single-grain discs (Bøtter-Jensen et al., 2000); care was taken to ensure that there was just one grain per hole. The pIRIR signals of individual grains were measured on a Risø automated TL-DA-20 reader. Irradiations were carried out using a calibrated $^{90}\text{Sr}/^{90}\text{Y}$ beta source. Stimulations were

conducted using infrared (870 nm) light-emitting diodes (LEDs) and a focussed infrared (832 nm) laser for measurement of the IRSL and pIRIR signals. The ‘blue’ luminescence emissions were detected through Schott BG-39 and Corning 7-59 filters using an Electron Tubes Ltd 9235QA photomultiplier tube. Measurements followed the pIRIR procedures outlined in Table 3.

The pIRIR signals of a total of 900 grains were measured from UK16-7: 200 from the ‘K-rich’, and 700 from the ‘Na-rich’, feldspar fractions. Many more grains ($n = 3,700$) were measured from LBB15-6: 1,100 and 2,600 from the ‘K-rich’ and ‘Na-rich’ feldspar fractions, respectively. Grains were rejected if (1) the initial pIRIR test dose to the natural (T_n) signal (step 8 in Table 3) was $<3\sigma$ above its corresponding background count, (2) the relative standard error on T_n was $>25\%$, (3) the recycling ratio was outside the range of 0.9–1.1, and (4) the sensitivity-corrected zero dose signal was $>5\%$ of the sensitivity-corrected signal obtained for the highest regenerative dose (i.e., recuperation). For UK16-7, 59% ($n = 117$) and 21% ($n = 146$) of grains were accepted from the ‘K-rich’ and ‘Na-rich’ feldspar fractions. For LBB15-6, 4% ($n = 46$) and 1% ($n = 25$) of grains were accepted from these fractions. Grains that passed rejection criteria were mounted for QEM-EDS measurements, as described in Section 2.1. Some grains were lost or crushed during this process, and not mounted.

4.2. Characterisation of grains

Using the QEM-EDS procedure described in Section 3, we determined the K concentrations of all mounted grains from UK16-7 and LBB15-6. For UK16-7, $\sim 94\%$ and $\sim 97\%$ of grains from the ‘K-rich’ and ‘Na-rich’ feldspar fractions contained multiple mineral phases. For grains from the ‘K-rich’ feldspar fraction, 93% of grain areas were orthoclase/microcline, with the remainder composed of albite (6%), quartz ($<1\%$) and mica ($<1\%$). For grains from the ‘Na-rich’ feldspar fraction, orthoclase/microcline, albite, quartz and mica accounted for $\sim 66\%$, $\sim 24\%$, $\sim 9\%$ and $\sim 1\%$ of the grain areas. Less than 1% of grain areas were unclassified for both fractions. These unclassified pixels often occurred at boundaries of grains (e.g., Fig. 3b, top), or the boundaries between two phases (with the

exception of boundaries between orthoclase/microcline and albite phases; e.g., Fig. 3c, top), suggesting that mixed EDS spectra were obtained for these pixels, resulting in best spectral matches with a goodness of fit <95%.

For LBB15-6, some grains contained one phase (sanidine), but most grains (~96% and ~89% from the 'K-rich' and 'Na-rich' feldspar fractions) contained multiple mineral phases. In ~4% of grains, orthoclase/microcline and albite were present, exhibiting coarse perthitic textures. In ~18% of grains, 'orthoclase/microcline' and sanidine phases were present, probably as a result of diagenesis. For grains from the 'K-rich' feldspar fraction, combined orthoclase/microcline and sanidine, albite and quartz accounted for ~95%, ~1%, and <1% of the grain areas. Similarly, for grains from the 'Na-rich' feldspar fraction, combined orthoclase/microcline and sanidine, albite and quartz account for ~94%, ~2%, and <1% of the grain areas. Unclassified mineral phases were present in most grains, but comprise only ~4% of grain areas from both the 'K-rich' and 'Na-rich' feldspar fractions.

4.3. Distributions of K concentrations

Fig. 9a and b shows the distributions of whole-of-grain average K concentrations of grains from the 'K-rich' (orange) and 'Na-rich' (green) feldspar fractions of both samples as histograms. K concentrations of grains from the 'K-rich' feldspar fraction of UK16-7 (n = 89) range from 9.4 to 13.5 wt%, giving an arithmetic mean of 12.3 ± 0.1 wt%. K concentrations of grains from the 'K-rich' feldspar fraction of LBB15-6 (n = 27) range from 9.9 to 13.2 wt%, giving an arithmetic mean of 11.8 ± 0.2 wt%. There is no contamination of low-K (<9.4 wt% K) feldspar grains in either sample, so the density separations were reliable. K concentrations of grains from the 'Na-rich' feldspar fractions of UK16-7 (n = 91) and LBB15-6 (n = 18) range from 0.0 to 13.4 wt%. Both samples show significant contamination of the 'Na-rich' feldspar fraction by K-rich (>9.4 wt% K) grains; almost all of the grains from LBB15-6 are K-rich, whereas ~56% of the grains from UK16-7 are K-rich.

4.4. Post-IRIR T_n signal intensities and K concentrations

It is often assumed that the IRSL and pIRIR signals of multi-grain aliquots are dominated by K-rich feldspar grains, even in the presence of low-K feldspar grains (e.g., Huntley and Baril, 1997). Spooner (1992) showed, however, that low-K feldspar grains can have IRSL signal intensities similar to that of K-rich feldspar grains. Huot and Lamothe (2012) even found that the IRSL signals of some of their multi-grain aliquots were dominated by low-K feldspar grains. The measurement of paired pIRIR signals and K concentrations of individual luminescent feldspar grains from UK16-7 and LBB15-6 provides an opportunity to directly assess the relationship between pIRIR signal intensity and K concentration for these samples.

Fig. 9c and d shows the pIRIR T_n signal intensities of grains from UK16-7 and LBB15-6 as a function of their corresponding K concentrations. For UK16-7 (Fig. 9c), the T_n signal intensities of grains from the ‘K-rich’ feldspar fraction (orange filled circles; $n = 89$) range from ~ 130 to $\sim 24,000$ counts per 0.1 s of optical stimulation time ($\text{cts} \cdot 0.1 \text{ s}^{-1}$), but most T_n signals are $< 5,000$ cts, with only three much brighter grains. For grains from the ‘K-rich’ feldspar fraction of LBB15-6 (orange filled circles in Fig. 9d; $n = 27$), the T_n signal intensities range from ~ 110 to $\sim 1,550$ cts, with one much brighter grain ($\sim 9,900$ cts). If the K concentration of each grain is weighted by its respective T_n signal intensity (as it would be on a multi-grain aliquot; T_n -weighted mean), a value of $12.2 \pm 0.1 \text{ wt}\%$ is obtained for UK16-7 (orange stippled line in Fig. 9c), compared to the arithmetic mean of $12.3 \pm 0.1 \text{ wt}\%$. For LBB15-6, the corresponding values are $12.1 \pm 0.3 \text{ wt}\%$ (orange stippled line in Fig. 9d) and $11.8 \pm 0.2 \text{ wt}\%$ K. The T_n -weighted mean values for both these samples are in good agreement with the conventionally used value of $12.5 \pm 0.5 \text{ wt}\%$ K (Huntley and Baril, 1997). This is unsurprising since all of the grains were K-rich in both samples, and the range of T_n signal intensities relatively small.

Grains from the ‘Na-rich’ feldspar fractions (green filled circles in Fig. 9c and d) of both samples show very similar T_n signal intensity distributions to their respective ‘K-rich’ feldspar fractions. For grains from UK16-7 ($n = 91$), T_n signal intensities range from ~ 100 to $\sim 14,300$ cts. For grains from LBB15-6 ($n = 18$), T_n signal intensities range from ~ 80 to $\sim 1,200$ cts. This is unsurprising as these fractions

are dominated by K-rich feldspar grains (Section 4.3). When taking into account only those grains from UK16-7 that are classified as low-K feldspar grains, a similar range of T_n signal intensities of between ~ 100 and ~ 9200 cts is obtained. We infer that for these two samples, there is little correlation between pIRIR T_n signal intensity and K concentration, but this may be different for other samples. We do, however, note that there is a difference in the average pIRIR T_n signal intensities of the two samples: UK16-7 is dominated by orthoclase/microcline (Section 4.2) that has high sensitivity, while LBB15-6 is dominated by sanidine (Section 4.2) that appears to have lower sensitivity.

Figure 9: (a–b) Distributions of whole-of-grain average K concentrations of grains from the ‘K-rich’ (orange) and ‘Na-rich’ (green) feldspar fractions of (a) UK16-7 and (b) LBB15-6 as histograms. (c–d) Post-IRIR T_n signal intensities presented as a function of K concentration for the same grains and feldspar fractions of (c) UK16-7 and (d) LBB15-6 as in (a) and (b). The orange stippled lines indicate the T_n -weighted mean K concentrations of grains from the ‘K-rich’ feldspar fractions of both samples. The blue and pink shading in (c) and (d) show the cut-off (9.4 wt%) between K-rich (blue) and low-K (pink) feldspars based on a density separation of 2.58 g.cm^{-3} .

5. Conclusions

K concentrations of individual luminescent feldspar grains from ‘K-rich’ feldspar fractions can range from 0 to 14 wt% due to the variable compositions of feldspar phases, differing proportions of discrete feldspar phases, and/or the presence of other mineral inclusions in grains. When measuring the IRSL or pIRIR signals of individual feldspar grains, and interpreting the resulting D_e distributions, knowing the effect of variable K concentrations on the shapes and dispersion of the D_e distributions is important and useful. Knowing the distributions of K concentrations, and how to combine these values to calculate a sample-average internal dose rate for age determination, is also important. Having an automated technique that can classify the range of mineral phases present in feldspar grains, determine their area proportions, and obtain accurate whole-of-grain average K concentrations is desirable. We propose that QEM-EDS is such a technique if careful consideration is given to calibration, and the accuracy of derived K concentrations is tested using independent methods such as WDS.

QEM-EDS classifies mineral phases on the basis of their compositions, and produces grain maps typically comprised of thousands of pixels each that provide the spatial resolution and coverage of all mineral phases from which accurate whole-of-grain average K concentrations of multi-phase grains can be derived. Using our calibration, QEM-EDS cannot, however, classify mineral phases with heterogeneity on a scale finer than the interaction volume of 2–3 μm . In this study, the presence of such phases were negligible, but if unidentified mineral phases comprise larger proportions of grains in other samples, it may be necessary to use a different approach to classify these phases, and account for their contributions to the average K concentrations of the grains. QEM-EDS mineral classifications should also be supported by other analyses (e.g., WDS or EDS) or previous studies because QEM-EDS can obtain incorrect classifications if the mineralogy is unknown (e.g., Meyer et al., 2013; Fang et al., 2018). The use of a spectral fitting threshold at 95%, however, significantly reduces the likelihood of incorrect mineral classifications.

QEM-EDS is time-efficient and automated. A mapping step size of 5 μm provides a good compromise between time-efficiency and accuracy of whole-of-grain average K concentrations. Using this mapping step size, ~2,400 spherical grains of ~200 μm in diameter can be measured in 24 hrs, which is far more efficient than any other technique.

The calibration developed in this study makes it possible to determine K concentrations of feldspar phases with a precision of ± 0.2 wt% (at 2σ) using QEM-EDS. The accuracy and precision of QEM-EDS-derived K concentrations is, however, dependent on the suitability of the reference standards used to obtain reference spectra for the QEM-EDS calibration. In this study, the orthoclase/microcline and sanidine phases contained negligible concentrations of Ca, as did the orthoclase and sanidine reference standards. Most albite phases contained minor concentrations of K and Ca, similar to the albite reference standard. One albite phase contained a higher concentration of Ca, but contained a negligible K concentration, thus occurring strictly in the range of the albite–labradorite solid solution region. High temperature single-phase alkali feldspar crystals (sanidine, anorthoclase and albite) can, however, contain non-negligible proportions of Ca up to ~4 wt% (Fig. 1a; Parsons, 2010). Similarly, plagioclase feldspar crystals can contain non-negligible proportions of K up to ~4 wt%. If higher Ca or K concentrations are present in natural alkali or plagioclase feldspar crystals, respectively, a user should be able to observe Ca or K peaks in the EDS spectra, which should also result in spectral matches with a goodness of fit <95%. In such an instance, it may be necessary to establish a different calibration using reference standards with compositions more similar to the natural feldspars. Furthermore, the mica phases identified in this study occur in the celadonite–muscovite solid solution series, with K concentrations ranging from ~9.1 to ~9.8 wt%. Such a small range in K concentrations (and the minor area proportions of these phases in grains) means that it is unnecessary to obtain a QEM-EDS calibration for these phases, but in instances where minerals of more variable K concentrations comprise larger area proportions of grains, it may be necessary to obtain a calibration for these mineral phases.

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Table 1: Elemental concentrations (wt%) of feldspar reference standards used to obtain reference spectra for the QEM-EDS calibration.

Reference standard	O	Na	Al	Si	K	Ca	Fe	Ba
Orthoclase	45.99	—	9.69	30.27	14.05	—	—	—
Sanidine	46.28	2.23	9.93	30.23	10.05	—	0.14	0.98
Anorthoclase	48.11	6.39	10.98	30.89	2.69	0.94	—	—
Albite	48.76	8.60	10.34	32.03	0.18	0.09	—	—
Labradorite	47.08	3.23	15.10	25.34	0.34	8.43	0.29	—
Anorthite	46.13	0.39	19.07	20.57	—	13.64	0.48	—

Table 2: Summary of mineral phases and their area proportions, assumed densities and derived K concentrations based on QEM-EDS measurements of grains presented in Fig. 3. This information is used to calculate whole-of-grain average K concentrations in Nanomin[®].

Grain code from Fig. 3	Phase	Proportion (%)	Density (g.cm ⁻³)	K concentration (wt%)	Whole-of-grain average K concentration (wt%)
A	Orthoclase/microcline	86.4	2.571	11.9	10.5
	Albite	12.4	2.605	2.1	
	Quartz	1.1	2.620	0.0	
	Mica	0.1	2.871	9.5	
B	Orthoclase/microcline	67.1	2.565	13.0	8.9
	Albite	32.4	2.616	0.9	
	Quartz	0.4	2.620	0.0	
	Mica	0.1	2.856	9.6	
C	Orthoclase/microcline	18.0	2.568	12.5	2.8
	Albite	29.0	2.613	1.1	
	Quartz	49.8	2.620	0.0	
	Mica	3.2	2.844	9.6	
D	Sanidine	100.0	2.581	9.7	9.7
E	Sanidine	100.0	2.575	11.1	11.1
F	Combined sanidine and orthoclase/microcline?	100.0	2.573	11.3	11.3

Table 3: Post-IRIR procedures used to measure the pIRIR signals of individual grains from the ‘K-rich’ and ‘Na-rich’ feldspar fractions of UK16-7 and LBB15-6.

Step	UK16-7	LBB15-6
1	Natural or regenerative dose	Natural or regenerative dose
2	Preheat at 300°C for 10 s	Preheat at 320°C for 60 s
3	IR LED stimulation at 200°C for 200 s	IR LED stimulation at 100°C for 200 s
4	IR laser stimulation at 275°C for 1.5 s	IR laser stimulation at 275°C for 1.5 s
5	Test dose of ~55 Gy	Test dose of ~20 Gy
6	Preheat at 300°C for 10 s	Preheat at 320°C for 60 s
7	IR LED stimulation at 200°C for 200 s	IR LED stimulation at 100°C for 200 s
8	IR laser stimulation at 275°C for 1.5 s	IR laser stimulation at 275°C for 1.5 s
9	IR bleaching at 320°C for 100 s	IR bleaching at 320°C for 100 s
10	Return to step 1	Return to step 1