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Determining the K-content of single-grains of feldspar for luminescence dating

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ABSTRACT

Feldspars form a solid-solution series whereby the K-content may range from 0 to 14%. LA-ICP-MS measurements for density-separated single-grains of feldspar yielded realistic concentrations of K within the range of those naturally occurring, and also highlighted the difficulty in isolating the pure end members during density-separation. No direct relationship was found between the thermal stability of the infrared-stimulated luminescence (IRSL) signal and measured K-content of individual grains. However, the brightest IRSL and post-IR IRSL signals originated from grains with ~12% K-content. All grains giving a measurable signal had K-content between 6 and 13%, therefore it is suggested that an internal K-content of 10 ± 2% can be assumed for routine single-grain dating of density-separated K-feldspars.

1. Introduction

In depositional environments where incomplete bleaching is likely, single-grain analyses have proven to be a valuable approach to optically stimulated luminescence (OSL) dating (Duller, 2008). A major challenge for single-grain measurements using quartz is that commonly only 5% or fewer of the grains emit a detectable OSL signal, and in recent studies of glaciofluvial sediments from Chile as few as 0.5% of grains could be detected (Duller, 2006). The use of feldspar for luminescence dating is limited by concerns regarding the effects of anomalous fading (Wintle, 1973), however recent advances in laboratory protocols aim to circumvent the problem of fading by accessing a more stable signal (e.g. Buylaert et al., 2009; Li and Li, 2011; Thomsen et al., 2008, 2011). A challenge for single-grain dating is that the internal K-content of individual grains, and therefore the magnitude of the internal beta dose to the overall dose-rate, is variable between grains. Feldspars form a solid-solution series, ranging from anorthite ($CaAl_2Si_2O_8$), to albite ($NaAlSi_3O_8$), to orthoclase ($KAlSi_3O_8$). Physical separation of detrital grains on the basis of density is routinely performed to isolate the orthoclase end member (K-feldspar) for OSL analysis; however, the K-content of separated materials has the potential to range from ~2–12% (e.g. Huntley and Baril, 1997) because of the difficulty of separating albite from orthoclase. Thus, precise consideration of the internal K-content on an individual grain basis is essential for single-grain dating.

The measurement of bulk K-content using various geochemical methods such as atomic absorption spectroscopy (AAS) (e.g. Huntley and Baril, 1997) and beta counting (e.g. Li et al., 2011) has proven appropriate for multiple-grain samples; however, these techniques are not suitable for measurement of the K-content of single-grains. Previous attempts to directly measure the K-content of single-grain feldspars using quantitative methods are limited. The first measurements of internal K-content for single-grains of feldspar were performed on a late-glacial marine sand by Lamothe et al. (1994). Ten repeated microprobe measurements across the surface of eight grains (diameter of 500–1000 μm) were made using a ~5 μm spot-size. The mean K-content of grains was ~11.66% (Lamothe et al., 1994), and although these microprobe measurements advanced the quantification of internal K-content for individual grains, the ~5 μm spot-size meant that only a small proportion of the feldspar grains were analysed. The perthitic nature of naturally-occurring feldspars means that intergrowths of Na-rich exsolution lamellae may not have been picked out by the microprobe analyses and therefore that the measured K-concentration may not have been representative of the whole grain.

Zhao and Li (2005) have subsequently used an electron microprobe to measure K-contents from a density-separated (<2.58 g cm^{-3}) sediment sample and obtained concentrations of ~13–14% K for 16 extracted single-grains. Godfrey-Smith et al. (2005) also measured K in single-grains and found concentrations of ~12.5 ± 0.6% using microprobe X-ray fluorescence. In both studies by Zhao and Li (2005) and

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Godfrey-Smith et al. (2005), grains of high K-concentration were specifically selected for analysis and were therefore not representative of the K-concentration of the K-feldspar separate as a whole. The variability in the K-concentration of grains within density-separated fractions has been demonstrated by Barré and Lamothe (2010) by analysis of an archaeological sediment using scanning electron microscope (SEM) images. The K-contents measured ranged from ~4–12.5% and ~0–12.5% for the K-feldspar and Na-feldspar fractions, respectively (Barré and Lamothe, 2010). This is similar to the range of K-concentrations (2–12%) measured by Huntley and Baril (1997) from a number of sedimentary samples separated based upon density and magnetic properties.

Although largely appropriate, the methods used throughout the studies described above are impracticable for routine use due to the extensive sample preparation required. In contrast, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) requires virtually no sample preparation prior to the analysis of individual grains, because they do not require polishing or mounting in thin section for analysis. Willerslev et al. (2007) used LA-ICP-MS for single-grain K-content analyses but employed Ca as the internal standard, which consequently required coupled single-grain SEM measurements to obtain numerical values for K-concentrations. To avoid the need for SEM analyses, Si can be used as an internal standard because it has a near constant stoichiometry in alkali feldspars. In this study a newly adapted LA-ICP-MS protocol is used which has the potential of providing more efficient analysis, requiring minimal preparation prior to measurement to obtain quantitative estimates of K.

The aim of the present work is two-fold, (1) to provide direct analyses of individual feldspar grains using LA-ICP-MS, in order to measure the internal K-content of each grain, and (2) to explore the potential of using luminescence properties as an indirect method of assessing K-content. Dütsch and Krbetschek (1997) observed a relationship between K-content of feldspars and the wavelength of the peak in the radio-phosphorescence emission at 720 nm (the afterglow in response to irradiation), but equipment for measuring radio-phosphorescence is uncommon. Two alternative possibilities of indirectly assessing K-content include thermal stability (e.g. Tso et al., 1996; Li et al., 2011) and signal intensity (e.g. Huntley and Baril, 1997; Spooner, 1992). Previous experiments comparing thermal stability and signal intensity to internal K-content were based upon the analysis of multiple-grain samples; single-grains were not examined. The present study undertakes direct analysis of single-grains using a newly developed LA-ICP-MS protocol and assesses whether thermal stability and signal intensity relate to K-content for individual grains.

2. Equipment and sample description

2.1. LA-ICP-MS

LA-ICP-MS analyses (Si, K and Ca) were conducted using a Coherent GeoLas ArF 193 nm Excimer laser coupled to a Thermo Finnigan Element 2 sector field high resolution ICP-MS. Grains for LA-ICP-MS analysis were secured in the single-grain holders used for OSL measurements by an organic glue solution (1% PVA) to ensure that the grains were held in the mount during ablation. An 80 μm diameter laser beam was used for ablation at an energy density of 3 J/cm^2, firing at 3 Hz to create an aerosol for major element analysis using the ICP-MS. Analyses were performed in medium resolution, which reduces the sensitivity of the ICP-MS by approximately 90% compared to low resolution mode and prevents saturation of the detector by major element isotopes, whilst also providing sufficient mass resolution to resolve several interferences from element peaks. The selection of ^{39}K and ^{44}Ca isotopes for analysis maximised the signal-to-noise ratio above the instrument background, caused largely by Ar polyatomic species formed from the sample carrier gas. Since Si has a near constant stoichiometry within all alkali feldspars the intensities of ^{39}K and ^{44}Ca can be calibrated by normalisation to ^{29}Si as an internal standard. This removes the associated affects of changes in ablation characteristics between standards and grains, and is standard practise in LA-ICP-MS analysis (see Perkins and Pearce, 1995; Pearce et al., 2004). LA-ICP-MS analyses were performed under the measurement conditions presented in Table 1.

2.2. Luminescence equipment

All luminescence measurements were performed using a Risø automated TL/OSL single-grain system equipped with an infrared laser (830 nm; 150 mW) fitted with an RG-780 filter to remove any shorter wavelengths in addition to the blue filter pack (Schott BG-39, GG-400 and Corning 7-59) placed in front of the photomultiplier tube. Samples were mounted in aluminium single-grain disc holders and stimulated using an infrared laser for 2 s at 90% power. Grains were rejected based upon the signal intensity (<3 sigma above the background), maximum test-dose error (> 20%), recycling ratio (> ±10%) and recuperation (> 5%) (Murray and Wintle, 2000). After luminescence measurements the samples were viewed with a binocular microscope and data were rejected where more than one grain was present in a single hole (typically <60% of holes per disc contain only a single-grain prior to measurement) so that one can be confident that geochemical and luminescence data came from the same material.

2.3. Sample description

The sedimentary sample (GDNZ13) used throughout these tests was a coastal dune sand from North Island, New Zealand. The sample was treated with a 10% v.v. dilution of 37% HCl and 30% H_2O_2 to remove carbonates and organics, respectively. Dry sieving isolated the 180–210 μm diameter grains. Density-separation provided the <2.58 g cm^{-3} (K-feldspar) and 2.58–2.62 g cm^{-3} (Na-feldspar) fractions. Grains were not etched with hydrofluoric acid. K-concentrations of 6.2% (K-feldspar) and 0.6% (Na-feldspar) were measured using a Risø GM-25-5 beta counter to analyse a 0.1 g sub-sample of the separated material.

3. LA-ICP-MS measurement of K-content

LA-ICP-MS Ca and K analyses were calibrated against external standards of NIST-610 (see Pearce et al., 1997) and glass from the "Big Obsidian Flow", Newberry Caldera, Oregon, to provide chemical concentrations (in weight percent). The Newberry obsidian has a reported K-content of 3.5 wt% (Higgins, 1973). The homogeneity of the standard is demonstrated by the low relative standard deviation (~4%) of replicate LA-ICP-MS measurements (n = 25), making it an appropriate calibration standard for LA-ICP-MS. The instrument was tuned in medium resolution mode for this study to give ~350,000 cps for 73% SiO_2 and 2,500,000 cps for 3.5% K from the Newberry obsidian.

Table 1
Measurement parameters for isotopes analysed during LA-ICP-MS. The sample time (0.01 s) and samples per peak (100) was the same for all isotopes analysed.

Isotope	Accurate mass	Mass window	Segment duration (s)
^{29}Si	28.9760	10%	0.1
^{39}K	38.9632	5%	0.05
^{44}Ca	43.9549	10%	0.1