Ancient TL

# Methods Note: An analysis of potassium to rubidium ratios in shoreline sediments: implications for OSL dosimetry

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## 1. Introduction

An integral step in OSL dating is determining the amount of natural radiation to which a sample is subjected in a given amount of time while buried. This value is referred to as a sample's "environmental dose rate," and it is calculated based on the concentration of radioactive elements within the sample, as well as the cosmic ray dose at depth. The four elements of interest for this purpose are uranium (U), thorium (Th), rubidium (Rb), and potassium (K). There are a wide range of analysis methods that can provide concentrations for these elements; one that is frequently used for luminescence dating is gamma spectrometry. While this method is relatively efficient and easy, it has a disadvantage in that it can only measure radionuclides that emit gamma radiation while decaying, a caveat which results in an inability to measure Rb in a sample ($^{87}$Rb, the naturally occurring radionuclide of Rb, is a pure beta emitter). Since Rb concentration is not directly measurable via this method, its value has been commonly approximated by using the measured concentration of K and an assumed K:Rb ratio of 200:1 (Aitken, 1985, 1998; Warren, 1978).

A review of this 200:1 ratio reveals that it is based on measurements of K and Rb concentrations from several published papers from the mid-twentieth century (Warren, 1978). While the results of these past analyses do show a general convergence around a 200:1 ratio, the measurements themselves were only conducted on pottery, shales, clays, and a handful of tektite samples, as shown in Table 1. This is a spread of sample types that were selected for their relevance to TL dating of artifacts, but they do not encapsulate all of OSL's potential geological dating applications. More recent work with OSL dosimetry on shoreline sediments of Glacial Lake Agassiz in North Dakota and Minnesota, USA, and in the Great Lakes region in the northern United States suggested that sediments of this type deviated from the expected ratio. In this analysis, shoreline sand samples from glacial Lake Agassiz and the Great Lakes region were studied to determine if the archaeology-based 200:1 K:Rb ratio was also applicable to the geology-based samples of this type.

## 2. Analysis

For the purpose of comparing the assumed 200:1 ratio to the measured K:Rb ratio of the lake shoreline sediments, data from sets of samples used in past projects were compiled and analyzed. In total, 200 dose rate samples were included in the data set; 84 of these samples were collected from beach ridges and spit complexes from Glacial Lake Agassiz. A further 63 samples were taken from strandplains of Lake Huron, and another 53 originated from strandplains of Lake Superior. These samples were collected and analyzed over the course of 17 years.

The potassium and rubidium concentrations of each sample, measured in parts per million (ppm), were determined using instrumental neutron activation analysis (INAA), which involves irradiating samples with neutrons in fission reactors. Neutron irradiation generates new, less-stable radionuclides, which generally have significantly shorter half-lives than the target element's naturally occurring isotopes. The resulting decay of these generated radionuclides emit radiation that can be discerned and measured via gamma spectrometry. The generated radionuclides for the elements of interest in this study were Potassium-42 ($^{42}$K; half-life 12.355 hours) and Rubidium-86 ($^{86}$Rb, half-life 18.66 days). An overview of the INAA method can be found in Reeves & Brooks (1979).

From 2005 through 2020 samples were dried and prepared for INAA at the Optical Dating and Dosimetry lab at North Dakota State University and then sent for neutron activation (irradiation), gamma spectrometry, and data analysis at The Ohio State University Nuclear Research Laboratory (OSU NRL). OSU NRL measured the naturally occurring gamma

| Analysis | K:Rb Ratio (± Std. Dev.) | Sample Type | Sample Count |
|---|---|---|---|
| Tobia & Sayre (1974) | 238 ± 99 | Soils, clays, shales, and pottery (Egypt) | 58 |
| Bieber et al. (1973) | 222 ± 68 | Clays and pottery (Eastern Mediterranean) | 235 |
| Perlman & Asaro (1969) | ≈ 200 | Pottery (Peru, Egypt) | 39 |
| Pinson et al. (1965) | 200 ± 27 | Tektites | 54 |
| Taylor & Ahrens (1959) *in Pinson et al. (1965)* | 220 ± 50 | Tektites | 5 |

Table 1. Summary of past K:Rb analyses.

emission from $^{40}K$, rather than the $^{42}K$ generated radionuclide. From 2020 to the present INAA has instead been conducted by the North Carolina State University Nuclear Reactor Program (NCSU NRP). Dried samples were sent to NCSU NPR where they prepared the samples for neutron activation and analysis. Both facilities have pool-type research reactors. Additional information about their methodology can be found on the laboratories' websites (`https://reactor.osu.edu` and `https://nrp.ne.ncsu.edu`; June 22, 2022).

The potassium and rubidium data from these samples were used to numerically calculate the statistical mean and median of the K:Rb ratios, as well as the standard deviation and standard error. In addition to numerical analysis, the samples were also plotted on scatterplots to help visualize the spread of the data, arranged such that the slope of the line-of-best-fit approximated the average K:Rb ratio for each data set. All 200 samples were plotted together, but selected subsets of the data were also studied independently in an effort to identify any trends that may have arisen. This included separating the samples by lake, which is reflected by the data plotted in Figures 1 and 2.

Figures 1 and 2 present the results of this analysis on a scatterplot and histogram, respectively, while the calculated values are tabulated in Table 2. The average potassium to

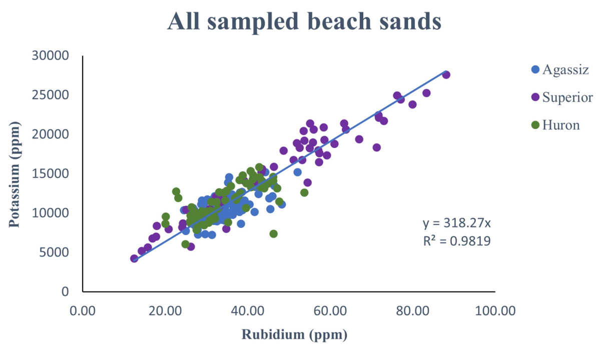


Figure 1. Collective scatterplot of all 200 samples, plotted by potassium against rubidium content. Average K:Rb ratio is represented by the slope of the line-of-best-fit at 318:1.

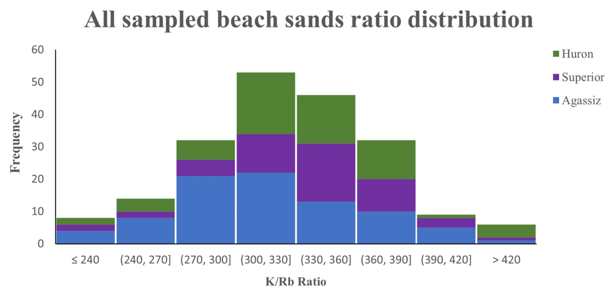


Figure 2. K:Rb ratio frequency distribution.

rubidium ratio of all samples in the data set was 328 ± 3.6 (std. err). Each individual lake yielded similar values as well, with Huron and Superior averaging 336 ± 7.6 (std. err.) and 336 ± 6.0 (std. err.), respectively. Lake Agassiz had a lower K:Rb ratio, down to an average of 316 ± 5.0 (std. err.), but it still fell well within a standard deviation of the overall mean, which was 51.

## 3. Conclusion

Recall that the overall K:Rb ratio for all 200 samples was 328 ± 3.6 (Table 2), with the mean ratio of each individual lake falling well within one std. dev. (51) of the mean. This average is a considerable difference, 64%, from the ratio proposed by Warren (1978) for his review of pottery, clays, shales, and tektites. If we consider a generalized shoreline sample containing 1% K, 2 ppm Th, and 1 ppm U sampled at a depth of 1m below the surface and having an average water content of 8%, the revised K:Rb ratio would result in a 0.63% difference in the calculated beta dose rate and a 0.36% difference in the total dose rate for the sample. Although these differences are small, it is more applicable to estimate the K:Rb ratios based on data from similar analog materials. The results from this analysis suggest that the commonly assumed 200:1 ratio is not appropriate for approximating the Rb content of shoreline sediments of the Great Lakes and Glacial Lake Agassiz and that an actual measurement of Rb would be necessary if one strives to ensure maximum accuracy of

| Shoreline Data Set | Number of Samples | Mean K:Rb Ratio | Median K:Rb Ratio | Std. Dev. K:Rb Ratio | Std. Err. K:Rb Ratio |
|---|---|---|---|---|---|
| All Lakes | 200 | 328 | 326 | 51 | 3.6 |
| Agassiz | 84 | 316 | 310 | 46 | 5.0 |
| Superior | 53 | 336 | 341 | 44 | 6.0 |
| Huron | 63 | 336 | 331 | 61 | 7.7 |

Table 2. Summary of calculated data.

results. Furthermore, these results also indicate that analysis of K:Rb ratios in other sediment types used for OSL dating is warranted.

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