PRELIMINARY STUDIES OF COEXISTING MICRON-SCALE ZIRCON AND BADDELEYITE IN SILICEOUS ROCKS FROM THE BASAL ROOIBERG GROUP, BUSHVELD COMPLEX, SOUTH AFRICA

TEGTMEIER, Eric L.[1], BREARLEY, Adrian[1], ELSTON, Wolfgang E.[1], and SPILDE, Michael N.[2], (1) Department of Earth and Planetary Sciences, University of New Mexico, Northrop Hall, MSC03 2040, 1 University of New Mexico, Albuquerque, NM 87131, teggy@unm.edu, (2) Institute of Meteoritics, University of New Mexico, MSC03-2050, Albuquerque, NM 87131

Abstract

Rhodes (1975) cited evidence that the ≤5 km siliceous Rooiberg Group of the ~2.06 Ga Bushveld Complex, widely accepted as an epicrustal volcanic succession, originated as an impact melt. This proposal was widely rejected because French (1990) found no evidence for shock. This study revisits the impact hypothesis with focus on Zr-bearing phases in the basal ~130 m of the Rooiberg Group (for setting, see Elston and Tegtmeier, this session). The rocks contain ~75 wt % SiO_2 (in rhyolite range) and 200-300 ppm Zr (Schweitzer, unpubl. Pretoria PhD diss. 1998), but lack optically resolvable and extractable zircon. Characteristics which suggest quenching from abnormally high temperature include unusual quench textures and an absence of phenocrysts.

WDS Zr X-ray maps of samples from the basal Rooiberg, obtained by EM, located numerous <10 µm, unzoned, unshocked, and subhedral-anhedral zircon grains. Of 50 grains examined in ~2 cm^2 of sample, 8 were irregularly shaped, 3-8 µm long, and composed of intergrown zircon and baddeleyite (ZrO_2). A FEGSEM and FIB-TEM investigation of one of these composite grains has revealed several distinct subgrains of ZrO_2 with the same crystallographic orientation, ± 2-3°. Dark field STEM imaging shows that the ZrO_2 subgrains are irregularly-shaped, and are either fully or partially enclosed by metamict zircon, suggesting that zircon partially replaced the ZrO_2. EM analyses found > 2,000 ppm U in zircon, accounting for its metamict state in a > 2 Ga rock (Ewing *et al.* 2000).

Zircon-ZrO_2 associations have been cited as evidence for "impact induced high temperatures" (French and Koeberl, 2010). In all previous reports of this association in impactites, zircon is the primary phase, inherited from the target rock and dissociated to ZrO_2 and SiO_2 at ~1680°C. These preliminary results suggest that ZrO_2 is the primary phase in basal Rooiberg. Zircon may have replaced ZrO_2 by reaction, T ≤1680°C, or by later alteration. If confirmed, this would be the first example of primary ZrO_2 crystallized from a SiO_2-oversaturated melt at T >1680°C. All of our conclusions are preliminary. Ongoing work will examine additional grains, determine ZrO_2 crystal structure, and test alternative interpretations. For example, there is a possibility that the ZrO_2 was inherited, but, unlike zircon, ZrO_2 is a rare accessory phase.

Introduction

Here we present results from an ongoing investigation of recently discovered < 10 µm zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) pairs in samples of the Basal Rhyolite. The Basal Rhyolite represents the basal 130 m of the Rooiberg Group, the epicrustal rocks of the 2057 Ma Bushveld Complex of South Africa [1]. According to the impact hypothesis, the Basal Rhyolite represents a superheated impact melt that assimilated, a quartz-rich sedimentary component derived from the target rocks (Elston et. al., this session) [2]. Our current study aims to test the impact hypothesis by looking for evidence that zircon was subjected to pressure or temperature regimes only compatible with impact processes.

Analytical Methods

Zr X-ray maps were created on a JEOL 8200 electron microprobe at the University of New Mexico, with the following parameters: 20 Kv, 30 nA, focused beam, 4 µm pixel size, and a dwell time of 50 ms/pixel. Areas of high Zr concentration were then examined in greater detail to document the Zr-bearing phases present (Fig. 1). Zircons and zircon-baddeleyite pairs were identified and analyzed using a WDS method that minimized the interaction volume overlapping more than one phase. The parameters used in these measurements were: 15 Kv, 10 nA, and a focused beam. Two of the grains that were identified as containing zircon-baddeleyite pairs were then used to create TEM sections using a FEI Quanta 3D Field Emission Gun SEM/FIB at the University of New Mexico. A JEOL 2010 high resolution transmission electron microscope (HRTEM) and JEOL 2010F FASTEM field emission gun scanning transmission electron microscope (STEM/TEM) at the University of New Mexico were then used to analyze the TEM sections.

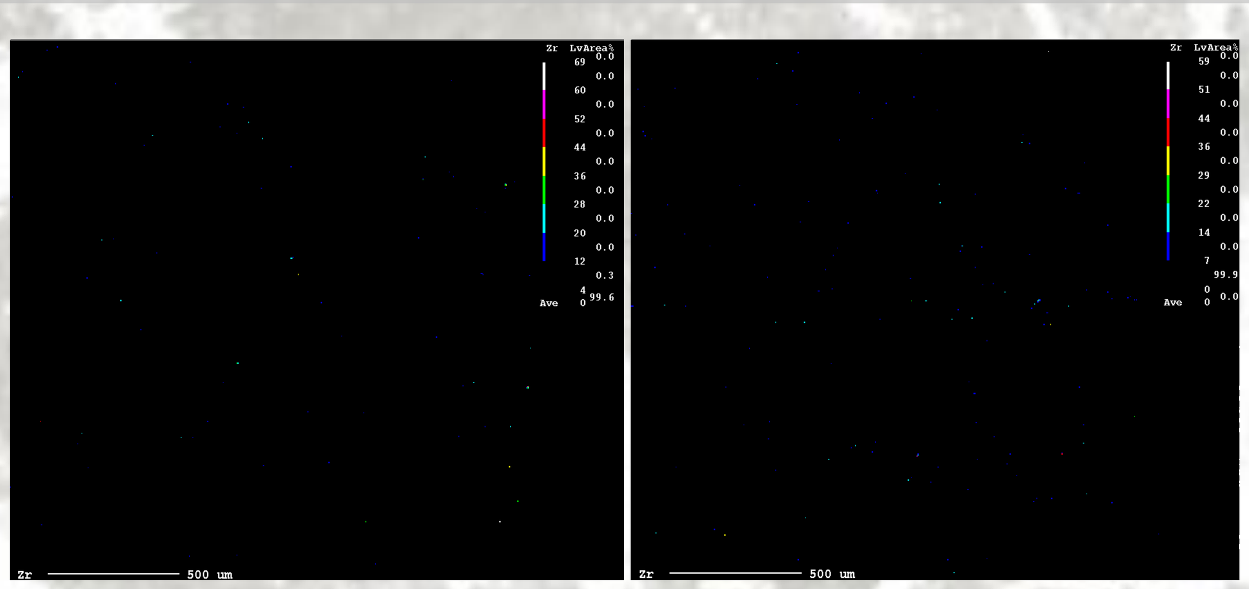

Fig. 1
2x2 mm X-ray maps indicate that Zr is located in grains <10 µm in size scattered throughout the sample. The highest detection levels (yellow to white) indicate either unzoned zircons 7-10 um in length or intermixed zircon-baddeleyite pairs 3-8 µm in length. The blue and green pixels indicate zircons that are 1-3 µm in length.

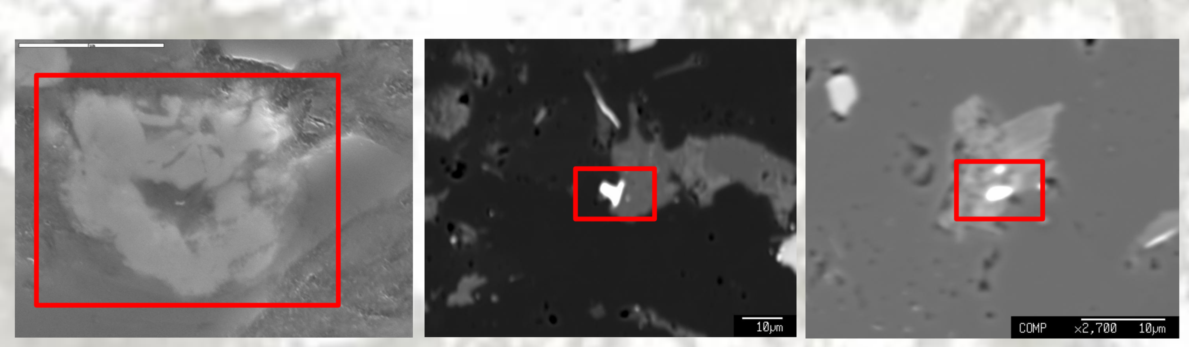

Figure 2. SEI and BSE images of zircon grains that do not occur with baddeleyite.

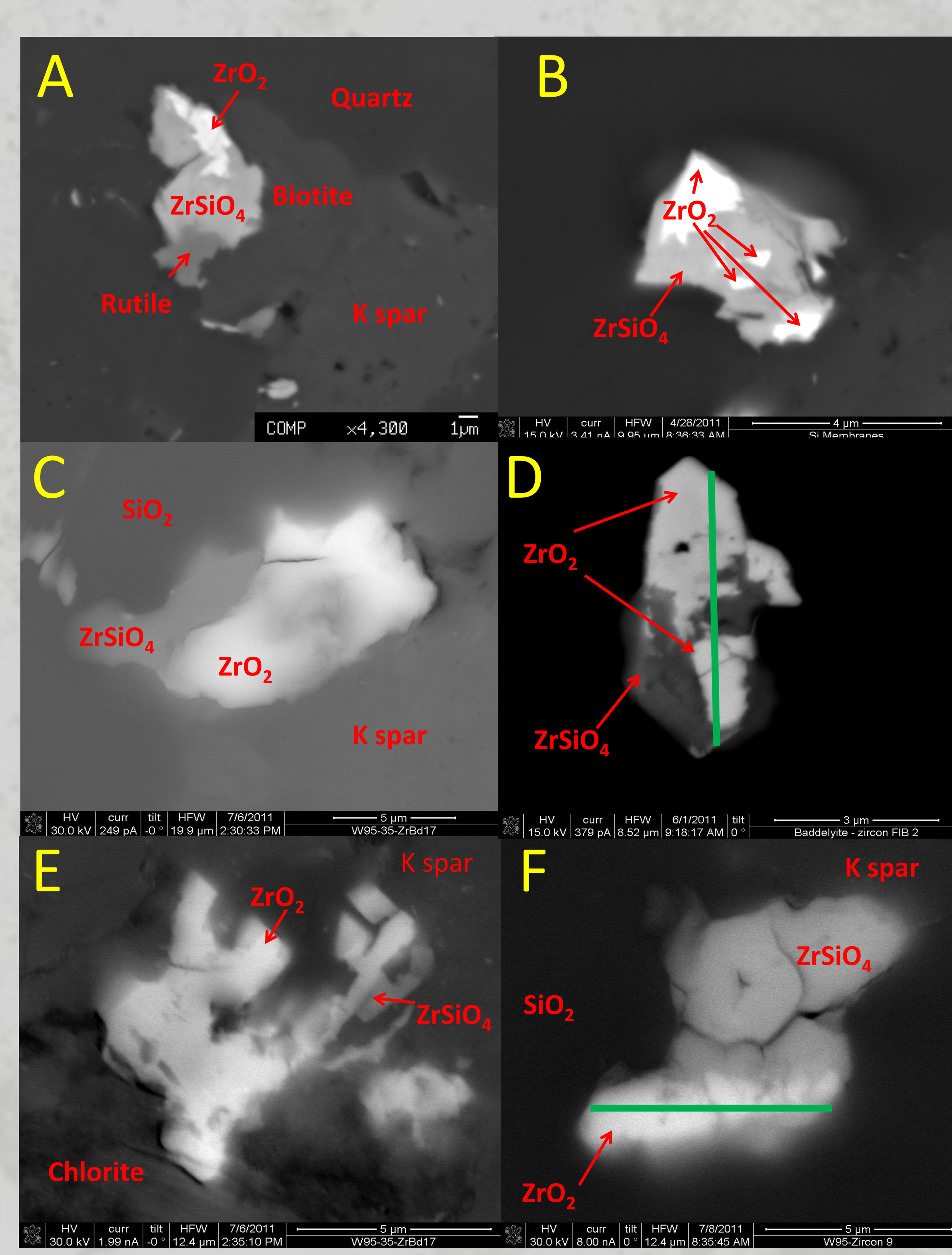

Figure 3. Intermixed zircon- baddeleyite pairs. Green lines indicate lines of TEM sections.

Petrologic observations and EM compositional data

•The Zr-bearing phases are extremely numerous yet very small, explaining why previous attempts to extract them were unsuccessful (Fig. 2 & 3).
•Intermixed zircon-baddeleyite show diverse morphologies. One grain (Fig. 3, E) appears to have a skeletal structure possibly indicative of rapid growth.
•Multiple grains (Fig. 3: A, B, C, and F) contain numerous embayments and facets that provide evidence for either resorption or physical weathering.
•Two grains (Fig. 3, B and D) appear to have maintained some indication of crystal structure, particularly in the baddeleyite, though they also show evidence for either resorption or weathering in places.
•The majority of zircon grains and zircon-baddeleyite pairs frequently occur along the boundaries between quartz and feldspar (orthoclase and/or albite).
•Other minerals that commonly occur in close proximity to Zr-bearing phases include rutile, biotite, and chlorite.
•The zircon grains often contain large fractures, likely due to metamictzation.
•High-resolution WDS analyses were difficult to carry out due to very small grain sizes which often resulted in phase overlap.

- **WDS data from zircons show enrichments (1-3%) in Fe, Al, Ca, Y and a depletion in Pb regardless of their proximity to baddeleyite. This indicates that the zircon was at one point metamict and subjected to hydrothermal alteration at ~ 200 °C, sometime after its formation [3]. U and Pb concentrations range from (0.2-0.6%) and (0.03-0.3%) respectively.**
- **Baddeleyite grains contain anywhere from (83-92%) Zr, (4-10%) Si, (1.8-3%) Ti, (1-1.2%) Fe, (0.8-1.8%) Hf, and (0– 0.3%) U.**

Acknowledgements

I would like to thank my advisor Wolf Elston for suggesting I locate Zr-bearing phases within this rock, it has turned out to be a most interesting, exciting, and enjoyable study. Special thanks to Michael Spilde and Adrian Brearley for the many hours of help with the instruments used in this study. Also a thanks is extended to the Rodney Rhodes Memorial Scholarship for their generous funding. Finally, I would personally like to thank my girlfriend Linda Dreeland for her great editing and intellectual support.

References: **[1]** C.J. Hatton and J.K. Schweitzer Evidence for synchronous extrusive and intrusive Bushveld magmatism Journal of African Earth Sciences Volume 21, Issue 4, November 1995, Pages 579-594. **[2]** W.E. Elston and E.L. Tegtmeier Setting and significance of zircon/baddeleyite in basal unit of Rooiberg Group, Stavoren Inlier, 2.06 Ga Bushveld Complex, South Africa Geological Society of America *Abstracts with Programs*, Vol. 43, No. 5, p. 305 **[3]** T. Geisler R, A. A. Rashwan, M. K. W. Rahn, U. Poller, H. Zwingmann, R. T. Pidgeon, H. Schleicher R and F. Tomaschek Low-temperature hydrothermal alteration of natural metamict zircons from the Eastern Desert, Egypt Mineralogical Magazine, June 2003, Vol. 67(3), pp. 485–508. **[4]** L.M. Heaman and A.N. LeCheminant Paragenesis and U-Pb systematics of baddeleyite (Zr02) Chemical Geology, *110 (1993) 95-126* **[5]** Verdel, C.; Mahan, K.; Guan, Y.; Eiler, J.; Wernicke, B. NanoSIMS 207Pb-206Pb dating of monazite, xenotime and baddeleyite American Geophysical Union, Fall Meeting 2007, abstract #V23B-1444

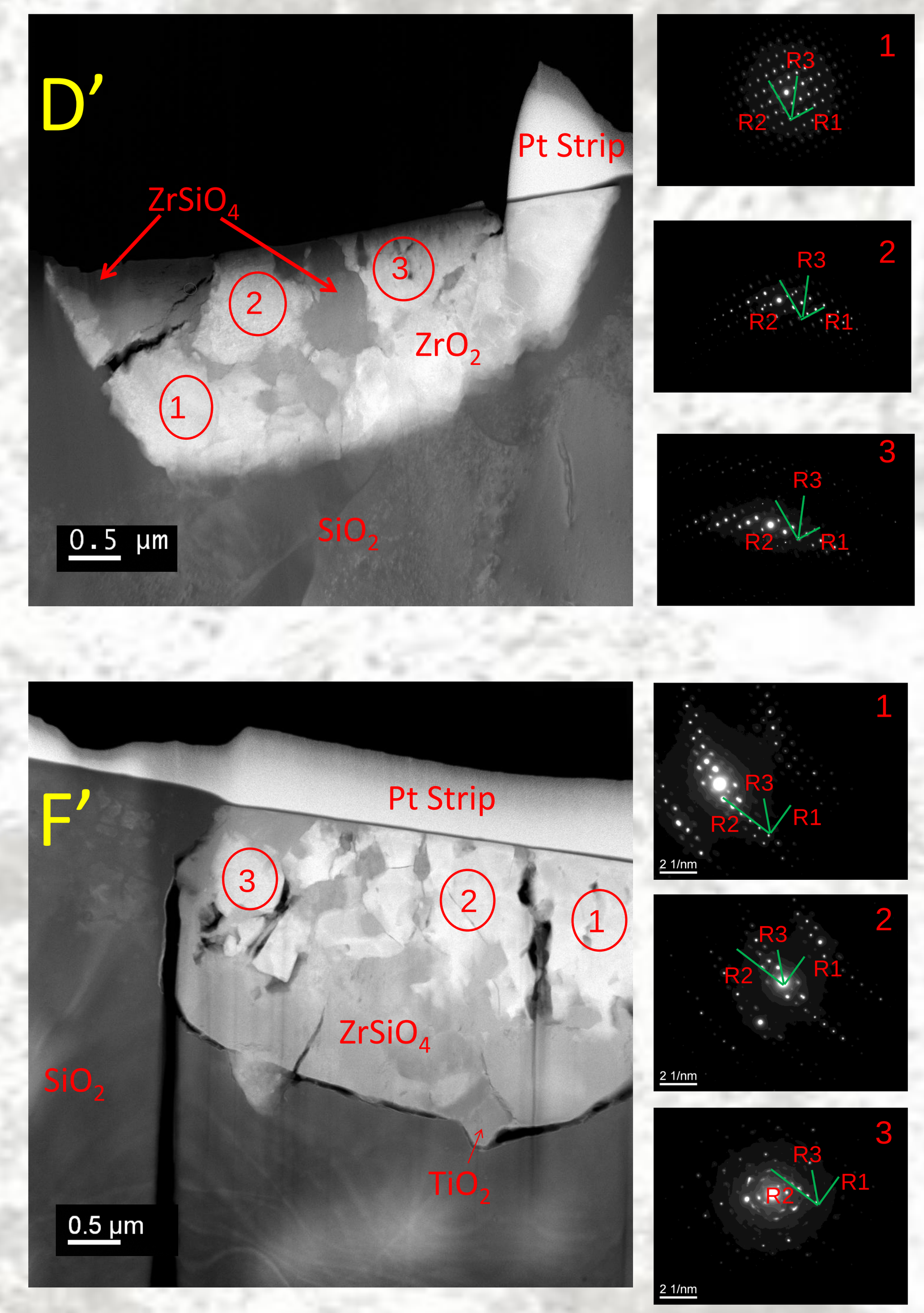

Figure 4. Dark Field TEM images D' and F' reveal the third dimension of grains D and F from Fig 3 along the green line. Red circles indicate where Selected Area Diffraction (SAD) patterns were created to determine the crystal orientation and structure of baddelyite.

Electron Diffraction Patterns (TEM)

The electron diffraction patterns created for Fig. 4, D' represent the monoclinic {101} zone axis of individual baddeleyite grains. The fact that variations in crystal orientation are very small is significant.

Fig. 4, F' was slightly thicker, requiring tilting of the beam to acquire a measurable zone axis. Second order Lau patterns are visible in SAD region 1, while second and third are visible in SAD region 2.

The circular pattern of blurred dots in image F' 3 is due to SAD overlapping with metamict zircon, thus detecting and incorporating its amorphous signal.

Textural Observations (TEM)

Dark field images highlight the complicated textural relationship between zircon and baddeleyite. The baddeleyite shows evidence of pervasive embayment by zircon. Several voids (black regions) and thickness variations (slight variances in brightness) suggest that the baddelyite contains numerous pore spaces.

Discussion

Our current TEM data is limited to two grains of intermixed zircon and baddeleyite from a single thin section. Based on electron diffraction patterns and textural evidence from these two grains, it appears that baddeleyite existed as the primary phase and was later replaced by zircon. To our knowledge, the reaction $ZrO_2 + SiO_2 \rightarrow ZrSiO_4$ taking place in a highly siliceous melt has never been documented and warrants further investigation. We have hypothesized two scenarios by which this reaction may have occurred, one of which is compatible with the impact hypothesis, while the other requires endogenic processes.

1. **The impact interpretation of these grains asserts that the ZrO_2 crystallized from a superheated impact melt > 1686 °C. Upon cooling, baddeleyite reacted with the melt to form zircon. This scenario requires that all Zr-bearing phases in the target rocks be completely melted before being incorporated into the Basal Rhyolite. The observation that all Zr-bearing phases in the samples lack zoning and are considerably smaller than 10 um may provide evidence that supports this interpretation. Indirect support for the superheated impact melt can be interpreted from unusual quench textures found in the rock. If the quench textures are shown to have formed from temperatures beyond known terrestrial siliceous volcanic processes, the impact scenario for the origin of the zircon-baddeleyite pairs would be reinforced.**

2. **The second interpretation does not require impact conditions for the presence of baddeleyite. Instead, it is hypothesized that baddeleyite was entrained into the siliceous melt, reacting with it to form zircon. Possible pre-Bushveld sources of baddeleyite are the Pretoria Group, a marginal marine transgression/regression sequence which also includes the 2222 Ma mafic to andesitic Hekpoort Formation. It is important to note that baddeleyite may not be as rare as once thought in mafic rocks [4]. Very small baddeleyite grains, similar in size to those observed in this study, may have been overlooked in mafic rocks when only using techniques such as optical microscopy. The possible evidence for physical weathering processes observed in the baddeleyites of this study may also support this interpretation (Fig. 3 C), though these features may have also formed by resorption.**

At present, there are two ways to determine which is the most likely interpretation for the observed coexistence of zircon and baddeleyite. One method requires a search of the Basal Rhyolite for a baddeleyite grain that is ~10 um in diameter, which can possibly be dated using a relatively new NanoSIMS technique [5]. If the date attained is older then the Bushveld Complex, it would prove that the baddeleyite was entrained from a pre-Bushveld source. However, if the baddeleyite is of Bushveld age, the entrainment of baddeleyite cannot explain the observed grains which would support the impact origin. Alternatively, Zr x-ray mapping of pre-Bushveld Complex sediments and volcanic units such as the Hekpoort formation would reveal whether small (< 10 um) baddeleyite grains are present. If small baddeleyites are discovered, it could be demonstrated that a population of small ZrO_2 grains were likely present and available for entrainment into a siliceous melt. If this search did not find baddeleyite present in significant amounts in any Pre-Bushveld rocks the impact interpretation would be the more likely scenario.