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The determination of erosion rates along the Vaal River in the Vredefort Dome, South Africa, using the cosmogenic nuclides \(^{10}\)Be and \(^{26}\)Al.

By

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DISSERTATION

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Co-supervisors: Dr. V.L Mbele / Dr. T.V Makhubela
Dedications

Dear God,

Thank you for carrying me through what has proven to be the most taxing, emotionally exhausting and potentially fulfilling experience of my life yet.

To the angels along the way,

Thank you for the paths crossed along this journey.

To my family,

I appreciate the support.

To Mama and Kokwani,

I hope you are proud.
Abstract
Landscape evolution studies using cosmogenic nuclides have been conducted in South Africa for the last two decades. The Vredefort Dome, which forms part of the world’s largest and oldest meteorite impact crater, has previously undergone extensive studies relating to its age, geology and geomorphology. However, no studies pertaining to the rate at which the rocks in the Vredefort Dome are being eroded are documented. The Vaal River flows in mixed bedrock-alluvial terrain through the Vredefort Dome, particularly in the Parys area, contributing towards the erosion and therefore landscape evolution in the dome. The character of the river is anabranching in the granitoid area, but then flows through a relatively narrow canyon in quartzites forming the collar of the dome. This study adopts the use of the cosmogenic nuclides $^{10}$Be and $^{26}$Al extracted from purified quartz samples, to investigate the erosion rates in the river and adjoining areas for both granitoid and quartzite bedrock along the Vaal River. The results of the study reflect that the erosion rates along the river for the quartzite and granitoid samples are ~ 3.08 and ~3.05 m/Ma respectively. Among the sampled quartzites, some indicate much lower apparent erosion rates, and this related to where they were sampled, with reference to their elevation above the river level (referred to as ridge quartzites). These quartzite samples were mainly collected from old, now elevated strath terraces, and in the logarithmic plot of $^{26}$Al/$^{10}$Be ratios vs $[^{10}$Be], they mainly plot on the constant exposure curve rather than on the steady erosion one. If the cosmogenic data on them are interpreted as yielding exposure ages (the preferred interpretation), then these range from 0.23 to 0.79 Ma. Among the sampled granitoids, there are samples (taken at a distance from the river bed) that, plotted in the same diagram, indicate constant exposure rather than erosion. Apparent surface exposure for these yielded an exposure age range of 0.27 to 0.37 Ma. It was expected that the granitoids would have erosion rates that are relatively faster than those of the typically more resistant quartzites. However, erosion rates in the river bed are equal for the two lithologies. This can be explained by the fact that the river is anabranching in the granitoids, changing its trajectory from time to time, while in the quartzites it is confined to a narrow, more permanent channel. If the river bed erosion in the quartzites were slower than in the granitoids, we would expect that a dam would have resulted in the central part where the granitoid rocks are found, but there is no evidence of this ever having happened. This points to a self-regulating mechanism. Determining the erosion rates allows for further understanding of anabranching in rivers, understanding the erosion mechanisms that are shaping the Vredefort Dome and
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CHAPTER 1: INTRODUCTION

1.1. Background to the study

The Vredefort dome, situated approximately 120 km south-west of Johannesburg, is the central uplift of the largest and oldest confirmed meteorite impact structure in the world (Reimold, Koeberl 2014). It was inscribed as a World Heritage site in 2005 by the United Nations Educational, Scientific and Cultural Organisation (UNESCO; whc.unesco.org, 2018). The age of this impact event is 2023 ±4 Ma, constrained from authigenic, unshocked zircon grains from pseudotachylitic breccias and impact melt rock known as the Vredefort Granophyre using the U-Pb isotopic results for concordant zircons by isotope dilution thermal ionization mass spectrometry (ID-TIMS) (Kamo et al., 1996; Moser, 1997; Graham et al., 2005). The Vredefort dome is geologically significant for two main reasons: 1. It is the oldest and largest impact structure on Earth, and 2. It represents a unique window into the geology of the upper and middle crust of the Kaapvaal craton. The rock deformation is regionally unique and astonishing and consistent with an enigmatic, cataclysmic origin (Gibson and Reimold, 2008; Reimold and Koeberl, 2014; Gibson and Reimold, 2015). The geology of the Vredefort dome and surrounding basin is well established (Stow, 1879; Daly, 1947; Dietz, 1961; Gibson et al., 1997; Gibson and Reimold, 1999; Lana et al., 2003a, b; Reimold and Gibson, 2006; Reimold and Koeberl, 2014). Archaean granite-gneiss basement core of the Vredefort dome is overlain by supracrustal sequences (in stratigraphic order) of the Dominion Group, Witwatersrand, Ventersdorp and Transvaal Supergroups (Figure 1.1; Reimold and Koeberl, 2014). In the southern part of the Vredefort dome, the basement and supracrustal strata are overlain by thick sediments of the Mesozoic Karoo Supergroup (Bisschof, 1999; Reimold and Koeberl, 2014; Gibson and Reimold, 2015). The Vredefort dome is deeply eroded (Reimold and Koeberl, 2014; Gibson and Reimold, 2015), with the near-circular structure at about 70 km wide (Kamo et al., 1996). Two billion years after the impact event, the structure no longer resembles the typical impact structures encountered on Earth and other planetary bodies. The original impact remnant has been levelled by post-impact tectonic evolution and a two-billion years erosion history (Henkel and Reimold, 1998). The original Vredefort impact crater is estimated to have been 250-300 km in diameter, based on regional distribution of shock-metamorphosed and brecciated material, shatter cones, and geophysical modelling (Therriault et al., 1997; Henkel and Reimold, 1998; Wieland et al., 2006). Even with most of the crater having
been eroded, there are effectively no published or known long-term bedrock erosion rates for the area.

![Image](image.png)

**Figure 3.1:** Simple general geology of the Vredefort Dome (modified from Reimold and Koeberl, 2014).

The Vredefort Dome is host to some fluvial systems (e.g. Klip and Wilge rivers that flow in a north-westerly direction) that contribute to shaping the landscape of the geological event. These are part of the catchment of the Vaal River, which traverses the northern part of the dome from east to west (Reimold and Koeberl, 2014). The anabranching and inherited meandering character of the Vaal River is distinctive and is an important contributor to erosion along the river (Gibson and Reimold, 2015), which influences changes to the wider landscape (Tooth and McCarthy, 2004; Gibson and Reimold, 2015). To develop an understanding of the evolution of the Vaal River and the Vredefort Dome landscape, measurement of bedrock erosion rates is essential. Cosmogenic nuclides provide an important tool for determining erosion rates and understanding the evolution of landscapes (Lal and Arnold, 1985; Kohl and Nishizumi, 1992; Hooke, 1994, 2000; Schaller et al., 2001, 2002; Decker et al., 2011; Granger, 2013).
1.2. Using cosmogenic nuclides to study landscape evolution

Cosmogenic nuclides are rare isotopes produced by cosmic ray interactions with atomic nuclei in the upper atmosphere and on the Earth’s surface (Gosse and Phillips, 2001; Dunai, 2010; Dunai and Lifton, 2014; von Blanckenburg and Willenbring, 2014). When primary cosmic rays in the atmosphere collide with atoms in the upper atmosphere, many particles possessing high kinetic energy are produced which are collectively termed secondary cosmic rays. Among these, neutrons are important, and can interact with atomic nuclei in processes referred to as spallation. When spallation reactions occur in the atmosphere, the products are referred to as meteoric cosmogenic nuclides (i.e. $^7$Be, $^{10}$Be, $^{14}$C and $^{36}$Cl; Gosse and Phillips, 2001; Dunai, 2010; von Blanckenburg and Willenbring; 2014). Nuclides that form by reactions of secondary cosmic rays with atomic nuclei on or near the surface are referred to as in-situ cosmogenic nuclides (see Figure 1.2). In-situ produced cosmogenic nuclides remain trapped in the minerals of rocks and sediment (von Blanckenburg and Willenbring, 2014). Some in-situ cosmogenic nuclides (e.g. $^{26}$Al and $^{10}$Be, this study) can be extracted by chromatography after the digestion of the target mineral and analyzed by accelerator mass spectrometry. Other cosmogenic nuclides can be measured in highly sensitive noble gas mass spectrometers following diffusion out of the host minerals by heating (i.e. Noble gas cosmogenic nuclides, $^{21}$Ne and $^3$He; Niedermann, 2002; Decker et al, 2011; Kounov et al., 2014; von Blanckenburg and Willenbring, 2014).

The measurement of cosmogenic nuclides produced in terrestrial samples is a good tool for quantifying continental erosion rates (Schaller et al., 2001,2002; Kounov et al., 2007; Decker et al., 2011), determining surface exposure ages in river terraces (Schaller et al., 2001,2002; Granger, 2013), dating various geologic events (Dirks et al., 2010; Bieman et al., 2014), quantifying landscape evolution (Flowers and Schoene, 2010; Erlanger et al., 2012; Chadwick et al., 2013; Scharf et al., 2013; Glotzbach et al., 2016) and making clear past climatic conditions (Corbett et al., 2013; Dosseto and Schaller, 2016). In fluvial geomorphology, cosmogenic nuclide studies can be used to interpret the history of river incision and aggradation by determining denudation rates (Schaller et al., 2001, 2002; Granger, 2013; von Blanckenburg and Willenbring, 2014).

The most commonly used cosmogenic nuclides in landscape evolution studies are $^3$He, $^{21}$Ne, $^{10}$Be and $^{26}$Al. Many landscape evolution studies in South Africa have used $^{10}$Be and $^{26}$Al in quartz from
sediment or bedrock outcrops (Dirks et al., 2010; Erlanger et al., 2012; Chadwick et al., 2013; Scharf et al., 2013; Bierman et al., 2014; Kounov et al., 2014; Dirks et al., 2016; Glotzbach et al., 2016). The advantage of $^{10}$Be and $^{26}$Al analyses for this purpose is that these nuclides are radioactive with (geologically speaking) short half-lives (1.39 and 0.7077 Ma, respectively), so that they are absent in minerals that have not been exposed at or near surface (Lal and Arnold, 1985; Lal, 1991; Kohl and Nishiizumi, 1992; Dunai, 2010). Other advantages of using quartz as a target mineral for analysis include that the mineral has a simple target chemistry, which allows for the theoretical calculation of $^{10}$Be and $^{26}$Al production rates (Kohl and Nishiizumi, 1992; Gosse and Phillips, 2001; Balco et al., 2008; Dunai, 2010), it is a common mineral (with the exception of $^3$He in pyroxene), is one of the most abundant silicate minerals on Earth and is robust and resistant to both chemical and mechanical weathering processes (Lal and Arnold, 1985; Lal, 1991; Kohl and Nishiizumi, 1992).

Figure 1.4: Summarised process of cosmogenic nuclide formation and production in the atmosphere and surface of the earth (von Blanckenburg and Willenbring, 2014).
The measurement of $^{10}\text{Be}$ and $^{26}\text{Al}$ has been made possible through the development of the accelerator mass spectrometer (Elmore and Phillips, 1987; Tuniz et al., 1998; von Blanckenburg and Willenbring, 2014). The essential idea behind the determination of erosion rates and concentrations of the cosmogenic nuclides is that; the longer the surface has been exposed to cosmic radiation, the greater the concentration of cosmogenic nuclides on that particular surface and as a result, the slower the erosion rates (Lal and Arnold, 1985; Gosse and Phillips, 2001; Bierman and Nichols, 2004; Dunai, 2010; von Blanckenburg and Willenbring, 2014).

1.3. **Aims and Objectives of the study**

The aims of this study are to understand the role of the Vaal River fluvial system in the landscape evolution of the Vredefort dome and to understand the relationship between the anabrancribing river style and the erosion of the two lithologies in the study area, granitoid rocks and quartzites. There is particular interest in understanding the rates of development of mixed bedrock-alluvial anabrancribing rivers in southern Africa and the Vaal River is an example of this river style (Tooth and McCarthy, 2004). Mixed bedrock-alluvial anabrancribing rivers occur as a result of a combination of factors that include erosion-resistant banks and poorly to moderately jointed/fractured granitoid outcrop (Tooth and McCarthy, 2004). The Vaal River in the Parys area is a prime example, particularly where it traverses the granitoids and quartzites that are typically jointed on scales of 1-3 m. The river is anabrancribing with multiple channels dividing and rejoining around islands of various sizes. Outside the boundaries of the granitoids and quartzites, both further upstream and downstream, the river adopts a bedrock-confined sinuous form. In particular, where the river traverses quartzites it begins to coalesce into a single-channel configuration. These resistant quartzites have acted as the lower base level for the anabrancribing atop the granitoids upstream, and incision rates through the quartzite have likely generated and driven upstream retreat of knickpoints.

The study aims to determine the relative erosion rates of these two different lithologies using cosmogenic concentrations of $^{10}\text{Be}$ and $^{26}\text{Al}$ extracted from quartz from the outcrops along the Vaal River in the study area. Quartz (SiO$_2$) is a suitable mineral for this study because it is a common mineral constituent of both granitoids and quartzites, both of which are dominant lithologies in the Vredefort dome area (Figure 1.1; Reimold and Koeberl, 2014; Gibson and Reimold, 2015). Knowledge of these relative erosion rates will help with our understanding of the
long-term development of the river and how the river has changed the broader landscape of the Vredefort dome. It is expected that, based on the properties of these lithologies and their *typical* resistance to weathering and erosion, that the erosion rates of the granitoids will be faster than those of the typically more resistant quartzites. One of the main questions we aim to address is how quickly the bedrock in the area is eroding. In this area, the river flows largely on the basement granitoids of the Archaean Basement Complex and also traverses the more resistant quartzite of the Dominion Group and West Rand Group of the Witwatersrand Supergroup (Reimold and Koeberl, 2014; Gibson and Reimold, 2015).

By constraining some of the regional erosion rates in the Vredefort dome area, this study will also contribute to the development of a broader regional database and contribute to the growing database of denudation rates in southern Africa. Knowledge of how rapidly the underlying bedrock along the river is being eroded (*this study*), combined with investigations of how the alluvial islands and/or floodplains along the river grow, erode and regrow (Tooth et al., *in progress*), will contribute towards understanding the overall development of the Vaal River. Determining the erosion rates in this particular area might also allow us to deduce the ages of the palaeo-terraces, by determining the exposure ages, that can be seen along the river channel and potentially quantify how quickly the river has been downcutting the bedrock of the Vaal dome.

The objectives of the study thus include:

- The sampling of the two lithologies that form the core and rim of the dome,
- The measurement of cosmogenic $^{10}$Be and $^{26}$Al concentrations from granitoid and quartzite bedrock samples along the Vaal River,
- The determination and comparison of the erosion rates along the valley of the Vaal River in the Vredefort dome, particularly in the Parys area,
- The determination of the ages of the paleo-terraces in the area.

**1.4. Outline of the study**

The structure of this dissertation is as follows:
• Chapter two describes the geology and geomorphology. It describes the general stratigraphy of the Kaapvaal craton, which the dome is found on and the stratigraphy within the Vredefort dome area. The chapter also describes the geomorphology that makes up and drives the landscape evolution in the dome.

• Chapter three describes the sampling in the study area and the methodologies that are adopted to achieve the aims and objectives. These include the collection of the samples; their comminution and the chemical processes used to separate and purify the quartz for measurement of $^{10}\text{Be}$ and $^{26}\text{Al}$.

• Chapter four reports and interprets the analytical results. It extensively looks into the results by describing the trends and observations which include the concentrations of $^{10}\text{Be}$ and $^{26}\text{Al}$, the erosion rates and apparent exposure ages.

• Chapters five and six discuss the results by looking at the erosion rates and exposure ages as calculated by the CRONUS-Earth online calculator. These are discussed extensively by also taking cognisance of the analysed concentrations. The discussion is detailed by making scientific conclusions by taking into consideration their lithologies and these interpretations are discussed in terms of the aims of the study.
CHAPTER 2: GEOLOGY AND GEOMORPHOLOGY

2.1. Geology of the Kaapvaal Craton

The Kaapvaal Craton (Figure 2.1) of southern Africa constitutes one of the oldest original mid-Archaean crustal fragments on the Earth (de Wit et al., 1992; Lana et al., 2003) with others including part of the Zimbabwe and Congo cratons. The craton stabilized between 3.7 and 2.7 billion years ago (de Wit et al., 1992). The craton and the adjacent Limpopo Belt to the northeast of it form part of the complete record of the evolution of the continental lithosphere (Hunter et al., 2006). The craton comprises large areas of granitoid gneisses with a number of infolded greenstone belts, along with their remnants, ranging in age from about 3.5-2.7 Ga (Brandl et al., 2006), the oldest of which is the Barberton Greenstone Belt (BGB) (Anhaeusser, 2006). The craton is subdivided into different sections. These are the Eastern-Southeastern, Northern and Northeastern, Southwestern and Central Kaapvaal Craton. The central part of the craton has geological features
that include the Johannesburg Dome, the Amalia Greenstone Belt, the Makoppa Dome, the Kraaipan Greenstone Terrane and the Vredefort Dome (Brandl et al., 2006).

A number of ultramafic and mafic intrusions (Anhaeusser, 2006) as well as many Archaean granitoid intrusions (Robb et al., 2006) have been emplaced into the Kaapvaal craton. These started from pre- 3.6 Ga (Eoarchaean) and went on to extend into the Late Cretaceous period (approximately 65 Ma). These intrusions are of a wide-range of lithological types which include mafic to ultramafic and granitoid-type rocks (emplaced between 3.6 and 2.5 Ga) with a variety of compositions and ages, and carbonatitic and alkali intrusions (Anhaeusser, 2006).

As the Kaapvaal craton (in particular the southern and central part) formed a relatively stable and rigid basement from the mid-Archaean onward, it is characterized by an unusually long record of supracrustal sedimentation and volcanism. The supracrustal rocks of the Dominion Group are the oldest at approximately 3.074 Ga old (Armstrong et al., 1991). The group comprises a bimodal sequence of basaltic andesite and felsic lavas with some secondary or minor rift-related clastic sediments. The thickness of the group can reach up to approximately 2.5 km in the Klerksdorp area towards the north-western part of the dome (Jackson, 1994). The inner collar rocks of the Dominion Group and lower West Rand Group of the Witwatersrand Supergroup show intermediate amphibolite-facies metamorphic grade (Bisschof, 1982; Jackson, 1992; Gibson and Wallmach, 1995).

Between approximately 2.97 and 2.71 Ga, an up to 7 km-thick sequence of clastic sediments was deposited to form the Witwatersrand Supergroup (Robb et al., 1997; Robb and Robb, 1998). The Witwatersrand Supergroup unconformably overlies basement rocks and greenstones, and also the volcanics and sedimentary rocks of the Dominion Group. The supergroup is in turn conformably and unconformably overlain by the volcanics of the Ventersdorp Supergroup (McCarthy, 2006). The basal West Rand Group of the Witwatersrand Supergroup comprises predominantly shallow-marine to subtidal argillaceous-arenaceous sediments (including massive quartzites), whereas the younger Central Rand Group is different as it comprises mainly of quartzites and conglomerates (McCarthy, 2006). Witwatersrand sedimentation was terminated at 2.714 Ga (Armstrong et al., 1991) by the eruption of tholeiitic flood basalts of the Ventersdorp Supergroup followed by up to 2 km of more localized rift sediments and subsidiary felsic volcanics (Gibson and Reimold, 2001).
The sediments of the Transvaal Supergroup have been deposited in three basins: The Kanye in Botswana and the Griqualand West and Transvaal basins in northern and central South Africa (Moore et al., 2001). Sedimentation of the Transvaal Supergroup started at approximately 2.65 Ga, with much of the craton being covered by a shallow sea, from which up to 2 km of dolomites and iron formations were deposited. This was followed by the deposition of the 3 km-thick argillaceous-arenaceous Pretoria Group of quartzitic sediments, from approximately 2.35 – 2.1 Ga (Walraven and Martini, 1995). In the northern part of the Transvaal basin, the upper Transvaal Supergroup is intruded by the Bushveld Igneous Complex at approximately 2.06 Ga (Olsson et al., 2010), this resulted in tectonics essentially downwarping of strata towards the centre of the Bushveld Complex) that affected the Transvaal sediments in a large part of this basin. The western margin of the craton was affected by the tectonics of the Kheis orogeny as a result of the thrusting of the Blackridge Thrust Fault that acts as a boundary between the Keis terrane and craton (Hilliard, 1999; van Niekerk, 2006).

The Karoo basins developed in south-western Gondwana during the Late Carboniferous, encompassing not only southern Africa but also large areas of Antarctica and South America (Grab and Knight, 2015). The subsequent infilling of the basin resulted in a total stratigraphic thickness of ~12 km. Sediments of the Karoo Supergroup cover more than half of South Africa (~600,000 km²; Smith, 1993). The sedimentary succession of the Karoo Supergroup accumulated over a period spanning from the Late Carboniferous (0.3 Ga) to the early Jurassic (0.19 Ga). Climate change over this time period influenced sediment type, depositional environments and geological structures. The basal Dwyka group consists of glacial deposits, while the overlying Ecca group is dominated by shales (which are organic-rich particularly at the base) which host a number of economically exploited coal seams. Sandstones and shales dominate the overlying Beaufort Group. Striking sandstone landscapes/landforms are those associated with the Molteno, Elliot and Clarens Formations of the Beaufort and Stormberg Groups. Sediments of the Karoo supergroup were only tectonically affected during the accretion of the Cape Fold Belt in the south. They were unaffected in the dome area. Karoo sedimentation was terminated by the basaltic outpourings around 0.183 Ga which was associated with continental rifting. These also resulted in the abundant dolerite dyke and sills intrusions through the entire Karoo sequence (Grab and Knight, 2015) with this volcanic activity terminating at ~0.105 Ga (Eales et al., 1984).
The Vredefort dome in the central Kaapvaal craton is a near circular remnant area of approximately 40 km diameter of a meteorite impact, in which Archaean basement is exposed in the centre. This Archaean granite-gneiss basement is overlain by supracrustal sequences, in stratigraphic order, of the Dominion Group, Witwatersrand, Ventersdorp, Transvaal Supergroups, with some pockets of outcropping of the mafic-ultramafic intrusions (Anhaeusser, 2006). These units form a rim in which the strata are steeply dipping or even overturned (Reimold and Koeberl, 2014). This is considered to be the central uplift of an impact structure. The diameter of the actual crater would have been much larger, 200 km or more (Gibson and Reimold, 2015) before erosion. Flat-lying sediments of the Karoo supergroup overlie the southeastern part of the dome.

The 2.023 Ga (Kamo et al., 1996) old complex Vredefort impact crater exposes an approximately 40 km wide crystalline basement core of metamorphosed granitoids which, together with the Archaean and Palaeoproterozoic metasediments of the Kaapvaal Craton, stretch through approximately a third of the earth’s geological history (Gibson and Reimold, 2008). It has provided a unique window into the Archaean geology of the area and has allowed for detailed and extensive studies of more than a billion years of geological evolution of the deep crust of the Kaapvaal craton (Gibson and Reimold, 2001). In papers since the early 1980’s, Hart and co-workers (Hart et al., 1981, 1990a, b; De Wit et al., 1992; Tredoux et al., 1999; 2004; Moser et al., 2001; Flowers et al., 2003) suggested that the doming (and later erosion) exposed a complete and full section through the crust of the centre of the Kaapvaal craton (Gibson et al., 2005). The geology of the Vredefort Dome and surrounding Witwatersrand basin is well established (Stow, 1879; Daly, 1947; Dietz, 1961; Gibson et al., 1997; Bisschof, 1999; Gibson and Reimold, 1999; Lana et al., 2003a, b; Reimold and Gibson, 2006; Reimold and Koeberl, 2014).
2.2. Regional Geology

Figure 2.2: Geology of the Vredefort Dome showing study location. (Modified from Gibson and Reimold, 2015).

2.2.1. Basement rocks

The rock units occurring in the centre of the dome are mainly Archaean granitoids, most of which are considered to have crystallised from magmas deep below a volcanic arc about 3.1 Ga ago (Robb et al., 2006). These also include some large xenoliths of high grade metasediments and metavolcanics, interpreted as sea-floor basalts and mudrocks (Gibson and Reimold, 2015). Stepto (1990) divided the classification of the granitoids in the basement as the Outer Granite Gneiss (OGG), and the Inlandsee Leucogranofels (ILG). The basement, as a whole, comprises mostly deformed, upper amphibolite- to granulite-facies migmatitic gneisses, with some small granitoid bodies and meta-sedimentary and meta-volcanic granulite xenoliths (Slawson, 1976; Stepto, 1979; 1990; Hart et al., 1990a; Lana et al., 2003).
2.2.2. Mafic-ultramafic intrusions
The Vredefort dome has numerous Neoarchean to Mesoproterozoic ultramafic intrusions which comprise some sills and dykes. These were emplaced onto the core and collar rocks that make up the dome (Anhaeusser, 2006). In the dome, studies (Stepto, 1990; Bisschoff, 1999; Gibson and Reimold, 2001; Anhaeusser, 2004) have categorized the different intrusions based on whether they were emplaced before or after the Vredefort impact event. A set of what is termed “Primitive” mafic-ultramafic intrusions was recognized by Stepto (1990) which were emplaced into the core of the basement of the Vredefort dome. Mafic intrusions of sills and dykes of dolerite, amongst other lithologies such as norite and diabase, have been found to occur within the Transvaal Supergroup in the collar of the dome (Anhaeusser, 2006).

2.2.3. Dominion Group and Witwatersrand and Ventersdorp Supergroups
The metamorphosed layered sedimentary and volcanic rocks surrounding the core, belonging to the Witwatersrand, Ventersdorp and Transvaal Supergroups (thus ranging in age from 3.074 – 2.1 Ga). These form a 20-25 km wide collar. In the dome, the Dominion group occurs in the collar of the impact structure where a complete sequence of strata has been turned upside down. Metamorphosed basaltic andesitic and felsic lavas comprise a bimodal sequence, with some minor clastic sediments (thought to be rift-related) intercalated. The maximum thickness of the Dominion Group is ~400 m (Jackson, 1994), and it is wedged between the Archaean granitoid gneisses and the basal quartzites of the Witwatersrand strata (Marsh, 2006).

The Witwatersrand metasedimentary strata in the dome are exposed as part of the 20 - 25 km wide partially- to wholly tilted sequence which surrounds the Archaean basement core. The Witwatersrand strata is at a thickness of ~7km thick with the Ventersdorp Supergroup at ~18 km. (Gibson et al., 2000; Wieland et al., 2005). The overturning of the strata occurred as a result of the collapse of the central uplift of the impact structure, downwards and outwards under its own weight post the impact (Gibson et al., 2000; Gibson and Reimold, 2015). This was the last stage of formation of the dome. The Ventersdorp and upper Witwatersrand Supergroup rocks in the collar of the Vredefort Dome show a similar, lower-greenschist, metamorphic grade to their stratigraphic equivalents in the goldfields (Gibson et al., 1998; Law and Phillips, 2005).
2.2.4. Transvaal and Karoo Supergroups

The lower Transvaal dolomite rocks (Malmani Group) contain numerous stromatolitic units (Gibson and Reimold, 2001). In the dome, sills and dykes of doleritic, noritic, pyroxenitic and diabasic occurrences of Transvaal age have been noted (Anhaeusser, 2006). Deformation of the supergroup in the dome itself as well as up to 50 km to the NW of it has also been noted to be associated with the Vredefort impact which has left these rocks tiled (McCarthy et al., 1986).

The dome is well exposed in its northern and northwestern parts. However, in the southern part of the Vredefort Dome, the basement and supracrustal strata are overlain by thick flat lying sediments of the Phanerozoic Karoo Supergroup (Bisschof, 1999; Lana et al., 2004; Reimold and Koeberl, 2014; Gibson and Reimold, 2015).

2.3. Geomorphology and Landforms of the Vredefort Dome

The geomorphological evolution of the Vredefort dome gives a glimpse into the environmental changes in southern Africa extending back 0.3 Ga. The Vredefort impact event is estimated to have left a crater that was originally at least 250 km wide and more than 1 km deep. The crater has since been removed by erosion which has resulted in only the central uplift being visible today (Gibson and Reimold, 2015). Estimates determined from the study of post-impact metamorphic parageneses in the rocks of the dome (Stevens et al., 1997; Gibson et al., 1998) show that there has been erosion of between 7 and 10 km since the impact event occurred (Lana et al., 2004). Palaeotectonics and land surface denudation long-term patterns of which have been studied play a significant role in the landscape evolution of Vredefort (Grab and Knight, 2015).

The drainage of the dome area is dominated by the Vaal River, which flows through it from the east to the west (Reimold and Koeberl, 2014; Gibson and Reimold, 2015) and plays a role in the landscape evolution of the dome. The river borders the North West and Free State provinces and is bound by a unique 100 km-long crescent of ridges and valleys (formed in the collar sequence) near the towns of Vredefort and Parys. At a macroscale level, the river shows a strong meandering character with an average gradient that drops approximately by 1 m every 1.5 km across the dome. It is also characterized by a series of local base levels marked by small rapids formed in the resistant bedrock. This is consistent with an inherited drainage pattern and explains why the river flows into and out of the Vredefort area. The current path the channel follows is strongly controlled by underlying geology (Gibson and Reimold, 2015). This is consistent with the factors determined
to be the drivers that control the anabraching character of the river in the study area (Tooth and McCarthy, 2004). The current erosion cycle is revealing an older, Permian aged glacial landscape that has been slightly modified by Mesozoic and Cenozoic erosion related to the Vaal River. The potholes in the area are evidence that suggests that the river was once larger than it is at present (Gibson and Reimold, 2015).

Figure 2.3: Hydrology map showing the Vaal River and two prominent sampling locations along the channel, Vredefort Dome.

Downstream of Kommandonek (Figure 2.3) the river flows across the strata of the inner collar and is deflected by the buttress of the Upper Witwatersrand Supergroup. Upstream of this locality, within the granitoid core, the effect of the foliation and fault related fractures can be seen in the anabranching observed around and downstream of Parys. The overall drainage pattern observed in the core of the dome is considered dendritic. Halfway between the town of Parys and Kommandonek, where the river re-enters the collar, the northeast bank of the river comprises a pavement with large potholes 2–3 m in diameter and over 1.5 m deep (Figure 2.4; Gibson and Reimold, 2015).
Tectonic history and long-term patterns of surface denudation are key controls on the geomorphology of Vredefort (Grab and Knight, 2015). Shuttle Radar Tomography Mission (SRTM) images show the difference in the landscapes of the ridges and valleys in the dome, where the core of the dome has mostly gentle topography at an elevation of approximately 1,400 metres above sea level (m a.s.l.) that starts rising to approximately 1,5000 m a.s.l. towards the west and northeast towards the collar rocks. Topographic relief is subtler and gentler away from the river channel towards the south. Some small dome-shaped hills exposing granitic bedrock rise up to 30 m above their surroundings. These dome-shaped granite hills of the core have locally preserved striations, which have been interpreted as glacial features caused by rock fragments being carried in moving ice during the Permian Dwyka glaciations. Towards the southwest and southeast both the maximum elevation and relief decline, before the rocks disappear beneath the Karoo strata (Gibson and Reimold, 2015).

Unlike in the Witwatersrand region, the Vredefort ridges are notably disjointed and, in some places, sinuous as a result of the displacement of faulting that occurred during the formation of the dome. All the ridges are formed by resistant quartzite outcrops (e.g. at the Kommandonek sampling
location), and the valleys are underlain by meta-shale, meta-basalt and/or meta-dolerite rocks that are more prone to chemical weathering processes. The relative differences in the compositions of these rocks play a significant role in the topography that can be seen in different parts of the dome (Gibson and Reimold, 2015).
CHAPTER 3: SAMPLING AND METHODOLOGIES

This chapter describes the sampling, laboratory and data reduction methods for determining the erosion rates and exposure ages used in the study. The physical and chemical preparation of the samples and chemical extraction of the isotope oxides by means of chromatography are described first and finally the data analysis after the samples are analysed for their isotopic concentrations by Accelerator Mass Spectrometry is summarized. The online erosion rate calculator cosmic-ray-produced nuclide systematics on Earth (CRONUS) is also explained as a necessary tool for interpreting erosion rate concentrations (Balco et al., 2008).

3.1 Samples studied

Fourteen samples of bedrock granitoid and quartzite (Table 3.1) were sampled in August 2012 along and near the Vaal River in Parys by Professor Stephen Tooth of Aberystwyth University. The samples were collected in two prominent areas along and near the river to represent the two lithologies that form part of the landscape of the study area (Figure 3.2). The anabranching character of the Vaal River in the dome in the sampling location sets it apart from other parts of the river in the dome (Figure 3.1) and this is why the samples were collected in this particular location.

3.1.1. Quartzite ridge samples

Four samples were collected on this site. Samples Vaal 1 to Vaal 4 were collected in the Kommandonek area, from outcrops on the quartzite ridge approximately 40 m above the current river level (Figure 3.3). At this location, the river cuts through the quartzite unit and the collar rocks of this unit make up the resistant ridge. This ridge is no longer flooded and is highly unlikely to be inundated during present-day floods. Since the area is not at the modern-day river level, the apparent erosion rates measured from these outcrops are expected to be lower than those of outcrops at the river level. The samples were collected as follows:

Vaal 1: Four pieces of sample were collected on a relatively flat location from a small pedestal on a strath terrace surface (Figure 3.5A).
Vaal 2: The sample was taken from the outcrop on the edge of a mini-strath. A steep cliff lies ~ 5 m to the south, recording a drop from the mini-strath above (Figure 3.5B).
Vaal 3: The sample was taken from the outcrop on the rock edge of a mini-strath. Small bushes lie immediately adjacent to the north. A steep cliff lies ~ 20 m south making a drop from the mini-strath where Vaal 2 was taken (Figure 3.5C).

Vaal 4: The sample was taken on a rock edge on a mini-strath. A steep cliff also lies ~ 20 m south, marking a drop from the mini-strath above. To the north is an even slope down the ridge to towards the current river level (Figure 3.5D).

Figure 3.4. is a topography sketch of the quartzite sampling locations with respect to their elevations. It shows the difference in the elevations and therefore the topography between the two groups of quartzite that were sampled. Elevation plays a role in the determination of erosion rates and exposure ages.

Table 3.1: Site specific data of quartzite and granitoid samples studied.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lithology</th>
<th>Latitude (DD)</th>
<th>Longitude (DD)</th>
<th>Sample Thickness (cm)</th>
<th>Elevation (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaal 1</td>
<td>Quartzite</td>
<td>-26.88547</td>
<td>27.35634</td>
<td>5.2</td>
<td>1376</td>
</tr>
<tr>
<td>Vaal 2</td>
<td>Quartzite</td>
<td>-26.88507</td>
<td>27.35669</td>
<td>9.2</td>
<td>1361</td>
</tr>
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<td>Vaal 3</td>
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<td>-26.88476</td>
<td>27.35693</td>
<td>6.8</td>
<td>1351</td>
</tr>
<tr>
<td>Vaal 4</td>
<td>Quartzite</td>
<td>-26.88458</td>
<td>27.35704</td>
<td>8.9</td>
<td>1349</td>
</tr>
<tr>
<td>Vaal 5</td>
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<td>-26.88390</td>
<td>27.35769</td>
<td>7.1</td>
<td>1334</td>
</tr>
<tr>
<td>Vaal 6</td>
<td>Quartzite</td>
<td>-26.88392</td>
<td>27.35777</td>
<td>5.5</td>
<td>1339</td>
</tr>
<tr>
<td>Vaal 7</td>
<td>Quartzite</td>
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<td>27.35777</td>
<td>8.3</td>
<td>1338</td>
</tr>
<tr>
<td>Vaal 8</td>
<td>Quartzite</td>
<td>-26.88396</td>
<td>27.35772</td>
<td>6.7</td>
<td>1336</td>
</tr>
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<td>Vaal 9</td>
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<td>27.38780</td>
<td>3.6</td>
<td>1347</td>
</tr>
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<td>Vaal 10</td>
<td>Granitoid</td>
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<td>27.38825</td>
<td>10</td>
<td>1350</td>
</tr>
<tr>
<td>Vaal 11</td>
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<td>27.38791</td>
<td>6.0</td>
<td>1350</td>
</tr>
<tr>
<td>Vaal 12</td>
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<td>27.38837</td>
<td>3.0</td>
<td>1344</td>
</tr>
<tr>
<td>Vaal 13</td>
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<td>1343</td>
</tr>
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<td>Vaal 14</td>
<td>Granitoid</td>
<td>-26.90195</td>
<td>27.38804</td>
<td>5.1</td>
<td>1346</td>
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</tbody>
</table>

Note: DD: decimal degrees.
Figure 3.1: Google Earth satellite image of the Vaal River in the Vredefort Dome, Parys showing the anabranching character of the river.

Figure 3.2: Google satellite image of the two sampling locations based on the lithologies. (Kommandonek – Quartzite; Stonehenge in Africa – Granitoids), Parys.
Figure 3.3: Google satellite image of the sampling location of the quartzite ridge samples, Kommandonek, Parys.
Figure 3.4: Field photographs showing the outcrops sampled. (A) Vaal 1: Quartzite sampled at the highest point of the study in Kommandonek. (B) Vaal 2: Quartzite sampled along the same ridge on the edge of a mini-strath. (C) Vaal 3: Quartzite sampled along the same ridge 10m below Vaal 02. (D) Vaal 4: Quartzite sampled 2m below Vaal 03 at the edge of a mini-strath along the same ridge. Photographs by Stephen Tooth.
Figure 3.5: Sketch of Topography based on quartzite elevation data (Not to scale).

Figure 3.6: Field photographs showing the outcrops sampled. (A) Vaal 1: Quartzite sampled at the highest point of the study in Kommandonek. (B) Vaal 2: Quartzite sampled along the same ridge on the edge of a mini-strath. (C) Vaal 3: Quartzite sampled along the same ridge 10m below Vaal 02. (D) Vaal 4: Quartzite sampled 2m below Vaal 03 at the edge of a mini-strath along the same ridge. Photographs by Stephen Tooth.
3.1.2. Quartzite along the Vaal River

Samples Vaal 5 to Vaal 8 were collected from the same quartzite unit cut by the Vaal River, but along the current river level. This part of the quartzite unit has been eroded by potholes and plucking of the bedrock. The samples, however, were not collected in the potholes and plucked depressions, but from the flat outcrop surfaces. These samples might be able to give an idea of the incision rate of the Vaal River through the quartzite unit. Comparison of erosion rates of these samples to those of samples Vaal 1-4 from the ridge, might demonstrate how the erosion rates have changed since the river incised further down. Each of the samples were collected as follows:

Vaal 5: The cohesive sample was taken from the edge of a plucked area of the outcrop. A large pothole is seen ~ 2 m west of the outcrop. An upstanding quartzite block forms a shelf up to 1.3 m high to the east of the sampling point. (Block shielding has been noted in the shielding survey and shielding correction) (Figure 3.6A).

Vaal 6 and 7: The samples were taken adjacent to each other on an “island” up to 1.3 m higher than the surrounding outcrop. Vaal 6 is very broken, whereas Vaal 7 is cohesive. (Figures 3.6B, 3.6C).

Vaal 8: The sample was taken from a plucked area next to a pothole. It was ~ 0.5 m higher than Vaal 5 but also on the lower part of the outcrop (Figure 3.6D).
Figure 3.7: Field photographs showing the outcrops sampled. (A) Vaal 5: Quartzite sampled along the current river level. (B) Vaal 6 & 7: Quartzite sampled along the current river level on a pedestal. (C) Vaal 8: Quartzite sampled next to a pothole along the current river level. Photographs by Stephen Tooth.
Figure 3.8: Field photographs showing the outcrops sampled. (A) Vaal 5: Quartzite sampled along the current river level. (B) Vaal 6: Quartzite sampled along the current river level on a pededstal. (C) Vaal 7: Quartzite sampled along the current river level on a pedestal. (D) Vaal 8: Quartzite sampled next to a pothole along the current river level. Photographs by Stephen Tooth.
3.1.3. Granitoid outcrops in the river

Samples Vaal 9 to Vaal 14 were collected from granitoid outcrops next to the modern river water level at the Stonehenge in Africa resort. They were sampled at the base of the first set of rapids upstream from the quartzite ridge. This was partly for easy accessibility reasons but also because this location is at the foot of outcrops showing pseudotachylitic veining, which are fluvially abraded and plucked with some minor local potholes. This location was also chosen because the granitoids are an integral part of the anabranching characteristic and they are representative of the granitoids that outcrop widely in the dome. The granitoid samples were collected along the river (Figure 3.6), and the locations are slightly spread out to give a representative indication of possible small-scale variation in the granitoid erosion rates. The samples were taken from flat outcrop, not in potholes or plucked depressions but should give an idea of the river of incision rates through the granitoids. It was anticipated that the erosion rates determined from Vaal 9 - 14 would be highly variable (i.e. reflecting differential histories of block removal) but overall, it was anticipated that the rates would be higher than those of the quartzite unit along the river (Vaal 5 - 8). Essentially, the erosion rates between all three sampling locations should be different, but collectively should be able to give an indication of the range of erosion rates along the Vaal River in this particular anabranching region of the river, in the Vredefort Dome, thus contributing towards understanding erosion along the river.

The samples were collected as follows:

Vaal 9: The sample was taken near the river level. On the adjacent edge of a sheet joint ~3cm thick, therefore, the area next to it had been plucked. The sample was covered by lichen, but the rock surface was abraded and polished. The adjacent rocks ~5m from the sampling location provide land shielding (Figure 3.8A).

Vaal 10: The outcrop is ~3m above the river level on jointed blocks near the lawn. This sample was the most weathered. It had red staining and a cracking surface. It was also very crumbly when sampled (Figure 3.8B).

Vaal 11: The outcrop was ~3m above the river level at about ~100m distance from Vaal 12. It was located on the edge of a sheet joint near an area with surface pitting. The surface of the sample is iron-stained but the rock beneath is fresh (Figure 3.C).
Vaal 12: The outcrop was near the river level. The surface is fluvially abraded and potholed. It is near the edge of a sheet joint and therefore, the surface immediately next to it had been plucked (~5m of rock remnant) (Figure 3.8D).

Vaal 13: The outcrop was located on top of a joint next to a block 1.5-2m above the river level. The surface is fluvially polished with strong patina staining. There is abundant plucking with blocks, boulders and localized potholing and sculptures and evidence of hydraulic jacking. The surface is pitted, which may be related to weathering that develops in boulders under local reed cover. Transient sediment cover may therefore characterize the sample (Figure 3.8E).

Vaal 14: The sample is located at an approximate 30m distance from Vaal 13 near the side of a jack-bound block. The surface is fluvially polished with light evidence of weathering. The sample also has some iron-staining and black patina “varnish” (Figure 3.8F).

Figure 3.9: Google satellite image of the granitoid sampling location in Stonehenge in Africa, Parys.
Figure 3.10: Field photographs showing the proximity of the sampling locations to the river level. (A) Vaal 9: Quartzite sampled near the river level. (B) Vaal 10: Granitoid sampled at a significant distance from the river channel. (C) Vaal 11: Iron stained granitoid sample collected towards the river from the lodge (D) Vaal 12: Granitoid sampled along the current river channel. (E) Vaal 13: Polished and stained granitoid sample collected on top of a jointed block. (F) Vaal 14: Slightly stained granitoid sample collected along the current river channel. Photographs by Stephen Tooth.
Figure 3.1: Field photographs showing the outcrops sampled. (A) Vaal 9: Granitoid sampled near the river level. (B) Vaal 10: Granitoid sampled at a significant distance from the river channel. (C) Vaal 11: Iron stained granitoid sample collected towards the river from the lodge (D) Vaal 12: Granitoid sampled along the current river channel. (E) Vaal 13: Polished and stained granitoid sample collected on top of a jointed block. (F): Vaal 14: Slightly stained granitoid sample collected along the current river channel. Photographs by Stephen Tooth.

3.2. Quartz separation and purification
The cosmogenic sample preparation methods used were adapted from the University of Vermont’s cosmogenic laboratory (Corbett et al., 2016). All the samples were cut, crushed and sieved at the iThemba LABS Facilities in Johannesburg. Fractions of grain sizes between 250 µm and 710 µm were rinsed in H₂O and dried prior to the commencement of the chemical quartz separation process. The separation and purification process involved leaching, etching, density separation and froth floatation processes described below (Appendix A).
3.2.1 Leaching and Etching

The samples were leached twice in a 1:1 1000 mL solution of milli-Q water (360 ml) and concentrated 32% hydrochloric acid (HCl; 640 ml). This step was carried out for the removal of grain-coating by oxides and to dissolve any carbonate material in the sample. Thereafter, the samples were etched in a 1:2 aqueous solution of concentrated hydrofluoric acid (HF) and concentrated nitric acid (HNO₃). The solution was made by mixing 210 ml of 48% HF and 100 ml of 55% HNO₃ in a 5000ml dispenser bottle of milli-Q water. The etching step was carried out once in a heated hotdog roller and twice in a heated ultrasonic bath and hotdog roller, with each step lasting for 24 hours. The purpose of this step was to remove all non-quartz minerals in the samples (e.g. feldspars) because most silicate minerals dissolve faster than quartz in a dilute HF solution (Corbett et al., 2016). Because of the robust nature of the quartz mineral, the acidic strength of HF etches away ~ 10% of the quartz grain coating and as a result, meteoric ¹⁰Be adsorbed on the outer parts of the quartz grains is removed as well. Some of the heavier minerals (e.g. ilmenite and rutile) and muscovite, do not efficiently get removed during HF/HNO₃ etching process. (Mathers, 2014). Hence, density separation and froth flotation were also used for purification of quartz. (See Appendix B(i) for step to step method).

3.2.2 Density separation and froth flotation

Density separation separates the dense minerals from relatively lighter ones in the samples (e.g. separating the lighter feldspars and quartz from the heavy ilmenite and rutile minerals). Lithium Metatungstate (LST) heavy liquid was used for density separation process. The LST heavy liquid is usually stored at a density of ± 2.85 g/cm³, but for these samples it was diluted to 2.7 g/cm³ so that both the quartz and feldspars would float, and all the other heavier minerals would sink. Feldspars have a density similar to that of quartz (~2.67 g/cm³) and hence the density separation process was not used to separate them. All the samples were treated to the same density separation method (Appendix B(ii)).

Froth floatation was used to separate feldspars and micas from the samples by using a soda carbonator. This step was carried out after density separation on the granitoid samples. This was done to separate the micas from the sample, as these were not successfully removed by the density separation process. See Appendix B(iii) for step by step details of the density separation and froth flotation methods.
3.2.3 Final HF/HNO₃ etch and quartz purity check

After all the separation and purification steps were carried out, the resulting ‘pure’ quartz was treated with a final etch in the premixed 1:2 HF/HNO₃ solution. This was carried out for 72 hours and then for one week straight in an ultrasonic bath (Appendix B(iv)). The samples were rinsed and dried in preparation for the quartz purity check to assess the effectiveness of the sample cleaning process.

Purity checks were carried out on the pure quartz samples to check if the cleaning process had been successful for the removal of other minerals. This was measured using inductively coupled plasma - optical emission spectroscopy (ICP-OES) in aliquots at the University of Johannesburg's Spectrum Analytical Facility. The purity check involved the digestion of an aliquot of 0.1 g of the clean samples in an HF solution of ultrapure 65% concentration and the preparation of the aliquots for the ICP-OES analyses. Step by step details of this process are detailed in Appendix C(i). The samples were analysed for the following elements; Al, Ca, Fe, K, Mg, Mn, Na and Ti in ppm. Results of the concentrations of the analysed elements of the purity check are summarized in Appendix C(ii).

Once the results of the ICP-OES check were satisfactory, the clean quartz samples were packed and shipped off to the University of Vermont, United States of America to undergo the column chromatography process.

3.3 Chemical separation of $^{10}$Be and $^{26}$Al by column chromatography

3.3.1 Sample digestion and column chemistry

The extraction process involves the digestion of the pure quartz samples by mass in concentrated HF that is heated in increments to a maximum of 135 °C for seven days. In most cases, this one included, a known quantity of $^9$Be is added as a carrier to the sample during the digestion process because Be is an ultra-trace element in the quartz mineral and since the accelerator mass spectrometric analysis determines abundance ratios but not absolute amounts of isotopes, the carrier is added as a comparison isotope to determine the amount of $^{10}$Be in the sample. An Al carrier is usually not necessary for the digestion of quartz. This is because quartz has sufficient natural aluminium in it for analysis (Finkel and Suter, 1993; Corbett et al., 2016). The process also involves a process of column chromatography (Figures 3.12, 3.13, 3.14) that involves the removal
elements like Ti during the cation column chromatography process (Figure 3.14) and the removal of Fe during the anion column chromatography process (Figure 3.13) in order to separate the isotopes of interest from the digested samples. A step by step instruction of how this is done is detailed in Appendix D.

3.3.2. Sample preparation for AMS analysis
The chromatography process resulted in hydroxide gels of Al(OH)₃ and Be(OH)₂ which are then ignited to result in Al₂O₃ and BeO that can be pressed into analysing steel cathodes and analysed by AMS. The dried hydroxide gels were packed into steel analysing cathodes at the University of Vermont’s cosmolab (Figure 3.15). The cathodes were cleaned and prepared there. Steel cathodes were used because the analysis is also for aluminium and using aluminium cathodes would create a systematic error during AMS analysis. The packed cathodes were shipped back to South Africa for analysis at the iThemba LABS AMS facility.

![Figure 3.12: Pure quartz samples digesting in concentrated HF.](image-url)
3.4 AMS Measurements and Computational Methods

The AMS analysis and sample reduction of the samples were carried out at iThemba LABS Gauteng. The samples were analysed by Dr. Stephan Winkler using the Kuni Standards calibration standards.
Computational calculations were used to reduce the raw isotopic results $^{10}\text{Be}/^{9}\text{Be}$ and $^{26}\text{Al}/^{27}\text{Al}$ ratios (Appendix E) from the AMS analysis into concentrations of the nuclides in quartz (in atoms/g; Balco, 2006). Once this has been achieved, the calculated concentrations and accompanying uncertainties can be used, together with the data in Table 4.1, as data input for the CRONUS-Earth Online calculator (http://hess.ess.washington.edu/math/v3/v3_erosion_in.html erosion rates and/or http://hess.ess.washington.edu/math/v3/v3_age_in.html exposure ages; Balco et al., 2008). These procedures are described in Chapter 4.

Figure 3.15: Sample of the steel cathodes that the dried hydroxide gel samples were dried and packed into for AMS analysis.
CHAPTER 4: RESULTS

In this chapter, I report the results from the data reduction methods used and analyse these results for trends and comparisons. There are three stages of data reduction that will be described in this chapter. The first is the reduction of the isotopic ratios yielded by the AMS analysis, using computations to determine the number of atoms/g of the two isotopes analysed for (Balco, 2006). Thereafter, the CRONUS-Earth online calculator, by Balco et al. (2008), using the Lifton, Sato and Dunai (LSDn) scaling scheme, is employed to determine the erosion rates and exposure ages and their uncertainties. The LSDn scaling scheme is used because it addresses any potential bias that was identified from previously used scaling factors (e.g. Lal and Stone, 2000; Desilets et al., 2006), that were categorised by the data which they were based on (See Lifton et al., 2014). The third involves the plotting of $^{26}$Al/$^{10}$Be vs. [$^{10}$Be] curves of Steady erosion and Constant exposure (banana plot; Figure 4.1.) using the determined concentrations. This provides a context enabling the comparison of the samples in terms of understanding the surface processes they document. The chapter will explore possible trends, similarities and differences between the collected samples and their results in order to determine whether there is a relationship between the samples based on their concentrations, erosion rates and their surface exposure ages. This will allow me to build scientifically plausible deductions that can explain the surface processes and landscape evolution that occurred in this area of study.

Analysis by AMS of the pure quartz samples results in $^{10}$Be/$^{9}$Be and $^{26}$Al/$^{27}$Al isotope ratio values. Results from this study’s analysis are reported in Appendix E. These results require reduction by converting them into $^{10}$Be and $^{26}$Al concentrations (in atoms/g) that are necessary for the calculation of erosion rates and surface exposure ages (Balco et al., 2008). Table 4.1 shows the resultant isotopic concentrations (atoms/g) as calculated using Balco (2006) and the data used for the erosion rate and exposure age calculations as required by the Balco et al. (2008) CRONUS-Earth online calculator for the calculations of erosion rates and surface exposure ages. The four right-hand columns report the concentrations of $^{10}$Be and $^{26}$Al and their uncertainties, obtained from the isotope ratios using Balco (2006). Also listed are the latitude, longitude and elevation, which are parameters required to calculate the local secondary cosmic ray (neutron and muon) fluxes at surface. The shielding correction is calculated from the surface topography. The reason for applying it is that a particular sample could be collected in a location that could be partially shielded from the cosmic-ray flux, either by surrounding topography or some extensively dipping
surfaces around it. The factor indicates what fraction of the secondary cosmic rays actually reach the surface (for instance in a valley, the value will be lower than on flat terrain, etc. Latitude, longitude, elevation, sample thickness and shielding correction together determine the production rate (for instance in atoms/g/day) that prevailed in the sample. Topographic shielding corrections calculations were done using skyline survey data of strike and dip angles measured by Professor Stephen Tooth during the sampling. The closer the calculated value is to 1, the more negligible the shielding. Table 4.1 reports the results of the topographic shielding corrections calculated using the shielding calculator [http://stoneage.ice-d.org/math/skyline/skyline_in.html](http://stoneage.ice-d.org/math/skyline/skyline_in.html). The measured concentrations are used together with the data in Table 4.1 to determine the erosion rates and/or surface exposure times.

For this study, erosion rates and surface exposure ages calculations were done by using $^{10}\text{Be}$ concentrations. This was done because using both the $^{10}\text{Be}$ and $^{26}\text{Al}$ concentrations for the same calculations would have been redundant as very similar values would result. This is shown by the fact that in Figure 4.1., the samples plot on or close to the steady state erosion and the surface exposure curves.
Table 4.1: Summary of sample data with nuclide concentrations and uncertainties.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lithology</th>
<th>Latitude (DD)</th>
<th>Longitude (DD)</th>
<th>Elevation (m)</th>
<th>Sample Thickness (cm)</th>
<th>Shielding Correction</th>
<th>$^{10}$Be (atoms/g)</th>
<th>$^{10}$Be (atoms/g)</th>
<th>$^{26}$Al (atoms/g)</th>
<th>$^{26}$Al (atoms/g)</th>
<th>$^{26}$Al/$^{10}$Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaal 1</td>
<td>Quartzite</td>
<td>-26.88547</td>
<td>27.35634</td>
<td>1376</td>
<td>5.2</td>
<td>0.99944</td>
<td>5.58E+06</td>
<td>1.32E+05</td>
<td>3.17E+07</td>
<td>6.13E+05</td>
<td>5.681</td>
</tr>
<tr>
<td>Vaal 2</td>
<td>Quartzite</td>
<td>-26.88507</td>
<td>27.35669</td>
<td>1361</td>
<td>9.2</td>
<td>0.99266</td>
<td>1.83E+06</td>
<td>9.99E+04</td>
<td>1.19E+07</td>
<td>2.82E+05</td>
<td>6.503</td>
</tr>
<tr>
<td>Vaal 3</td>
<td>Quartzite</td>
<td>-26.88476</td>
<td>27.35693</td>
<td>1351</td>
<td>6.8</td>
<td>0.99996</td>
<td>1.99E+06</td>
<td>1.07E+05</td>
<td>1.25E+07</td>
<td>2.98E+05</td>
<td>6.281</td>
</tr>
<tr>
<td>Vaal 4</td>
<td>Quartzite</td>
<td>-26.88458</td>
<td>27.35704</td>
<td>1349</td>
<td>8.9</td>
<td>0.99866</td>
<td>3.77E+06</td>
<td>1.18E+05</td>
<td>2.25E+07</td>
<td>4.68E+05</td>
<td>5.968</td>
</tr>
<tr>
<td>Vaal 5</td>
<td>Quartzite</td>
<td>-26.88390</td>
<td>27.35769</td>
<td>1334</td>
<td>7.1</td>
<td>0.99831</td>
<td>1.68E+06</td>
<td>1.07E+05</td>
<td>1.15E+07</td>
<td>2.74E+05</td>
<td>6.845</td>
</tr>
<tr>
<td>Vaal 6</td>
<td>Quartzite</td>
<td>-26.88392</td>
<td>27.35777</td>
<td>1339</td>
<td>5.5</td>
<td>0.99938</td>
<td>4.04E+06</td>
<td>1.14E+05</td>
<td>2.39E+07</td>
<td>4.98E+05</td>
<td>5.916</td>
</tr>
<tr>
<td>Vaal 7</td>
<td>Quartzite</td>
<td>-26.88392</td>
<td>27.35777</td>
<td>1338</td>
<td>8.3</td>
<td>0.99938</td>
<td>3.77E+06</td>
<td>1.22E+05</td>
<td>2.36E+07</td>
<td>4.91E+05</td>
<td>6.260</td>
</tr>
<tr>
<td>Vaal 8</td>
<td>Quartzite</td>
<td>-26.88396</td>
<td>27.35772</td>
<td>1336</td>
<td>6.7</td>
<td>0.99803</td>
<td>1.68E+06</td>
<td>1.14E+05</td>
<td>1.15E+07</td>
<td>3.11E+05</td>
<td>6.845</td>
</tr>
<tr>
<td>Vaal 9</td>
<td>Granitoid</td>
<td>-26.9019</td>
<td>27.3878</td>
<td>1347</td>
<td>3.6</td>
<td>0.99978</td>
<td>2.52E+06</td>
<td>1.12E+05</td>
<td>1.63E+07</td>
<td>3.48E+05</td>
<td>6.468</td>
</tr>
<tr>
<td>Vaal 10</td>
<td>Granitoid</td>
<td>-26.90187</td>
<td>27.38825</td>
<td>1350</td>
<td>10</td>
<td>0.99996</td>
<td>2.99E+06</td>
<td>1.09E+05</td>
<td>1.93E+07</td>
<td>3.97E+05</td>
<td>6.455</td>
</tr>
<tr>
<td>Vaal 11</td>
<td>Granitoid</td>
<td>-26.90149</td>
<td>27.38791</td>
<td>1350</td>
<td>6.0</td>
<td>0.99951</td>
<td>2.80E+06</td>
<td>1.14E+05</td>
<td>1.78E+07</td>
<td>3.80E+05</td>
<td>6.357</td>
</tr>
<tr>
<td>Vaal 12</td>
<td>Granitoid</td>
<td>-26.90230</td>
<td>27.38837</td>
<td>1344</td>
<td>3.0</td>
<td>0.99981</td>
<td>1.57E+06</td>
<td>1.10E+05</td>
<td>1.09E+07</td>
<td>3.11E+05</td>
<td>6.943</td>
</tr>
<tr>
<td>Vaal 13</td>
<td>Granitoid</td>
<td>-26.90207</td>
<td>27.38820</td>
<td>1343</td>
<td>5.9</td>
<td>0.99976</td>
<td>2.28E+06</td>
<td>1.24E+05</td>
<td>1.49E+07</td>
<td>5.58E+05</td>
<td>6.535</td>
</tr>
<tr>
<td>Vaal 14</td>
<td>Granitoid</td>
<td>-26.90195</td>
<td>27.38804</td>
<td>1346</td>
<td>5.1</td>
<td>0.99939</td>
<td>1.46E+06</td>
<td>1.05E+05</td>
<td>9.65E+06</td>
<td>2.59E+05</td>
<td>6.610</td>
</tr>
</tbody>
</table>

Note: DD: Decimal degrees
4.1. Concentrations (\(^{10}\text{Be}\))

The highest concentration among the quartzites is represented by Vaal 01 with the lowest represented by both Vaal 05 and Vaal 08. Vaal 03 and Vaal 07 have the same concentrations at 1.99E+06 atoms/g with a difference in their uncertainties where Vaal 07 has a slightly higher uncertainty. The highest concentration of the granitoids is Vaal 14 and the lowest represented by Vaal 10 and atoms/g. There are no clear trends that can be seen with the granitoids. Based on table (Table 4.2) that summarizes the calculated concentrations, it can be seen that the quartzite samples have a higher average concentration than the granitoid samples.

Table 4.2: Summary of average \(^{10}\text{Be}\) concentrations and ranges of the two rock types.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Range (atoms/g)</th>
<th>Average Concentrations (atoms/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartzites</td>
<td>1.68E+06 (± 1.07E+05) – 5.58E+06 (± 1.32E+05)</td>
<td>3.04E+06 (± 1.14E+05)</td>
</tr>
<tr>
<td>Ridge quartzites</td>
<td>1.83E+06 (9.99E+04) – 5.58E+06 (1.32E+05)</td>
<td>3.29E+06 (± 1.14E+05)</td>
</tr>
<tr>
<td>River bed quartzites</td>
<td>1.68E+06 (1.07E+05) – 4.04E+06 (1.14E+05)</td>
<td>1.895E+06 (± 1.14E+05)</td>
</tr>
<tr>
<td>Granitoids</td>
<td>1.46E+06 (± 1.05E+05) – 2.99E+06 (± 1.09E+05)</td>
<td>2.27E+06 (± 1.12E+05)</td>
</tr>
</tbody>
</table>
Samples that plot on both the steady erosion and constant exposure curves imply that the resultant erosion rate can be regarded as a minimum value (i.e. there might be a component cosmogenic nuclide from post-erosion exposure). On the other hand, the resultant exposure age, assuming zero exposure, is considered the maximum value.

Figure 4.1. shows the relationship between the samples by using the calculated concentrations on a plot of $^{26}$Al/$^{10}$Be ratios versus $[^{10}$Be] (both logarithmic), showing the curves describing steady erosion and constant exposure (also known as the banana plot).

As shown in Table 4.3, the same data can be used to calculate apparent erosion rates, or apparent exposure ages. In calculating the former, the assumption is made that the rate of erosion was steady in the recent geological past. For calculating the latter, it is assumed that the surface was uncovered in a single event, and that there was no erosion of the surface after that event. In reality many rock surfaces have undergone periods of steady erosion as well as periods of exposure with very little or no erosion. The two assumptions are thus endmembers for the history of an outcrop. If both
processes occurred, then the apparent erosion rate is a minimum value, while the apparent exposure age is a maximum value.

Plotting the sample values on the banana plot allows us to understand which samples experience either erosion and/or exposure. It appears that four different groups can be distinguished on the basis of how the samples plot relative to the curves. The first is clustered into Vaal 1, Vaal 7 and Vaal 10 which strictly plot along the constant exposure curve. Vaal 4, Vaal 6, Vaal 9 and Vaal 11 plot similarly along the constant exposure curve, however, their bottom boundaries (as a result of their uncertainties) overlap the steady erosion curve as well. Vaal 3 and Vaal 14 overlap both the steady erosion and constant exposure curves in equal measure but differ in their cosmogenic nuclide concentrations. The rest of the samples plot similarly, but with a bias towards constant exposure curve although steady erosion is by no means excluded. Samples Vaal 5 and Vaal 8 show identical values. Samples Vaal 1 through Vaal 4 are those that were taken on old strath terraces that are now variably elevated above the river bed. Vaal 6 and 7 were sampled on pedestals along the river bed. (Figure 3.6) Among these are the samples that most clearly plot on the constant exposure curve. These features, along with the position of some samples on the constant exposure curve, are considered further in the discussion section.

Table 4.3: Apparent erosion rates and apparent surface exposure ages results based on the $^{10}$Be data in Table 4.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Type</th>
<th>Erosion rates (m/Myr)*</th>
<th>Internal uncertainty (m/Myr)*</th>
<th>External uncertainty (m/Myr)*</th>
<th>Surface exposure ages (kyr)**</th>
<th>Internal uncertainty (kyr)**</th>
<th>External uncertainty (kyr)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaal 1</td>
<td>Quartzite</td>
<td>0.81</td>
<td>0.0263</td>
<td>0.0707</td>
<td>714.4</td>
<td>20.3</td>
<td>54.6</td>
</tr>
<tr>
<td>Vaal 2</td>
<td>Quartzite</td>
<td>2.79</td>
<td>0.1690</td>
<td>0.2480</td>
<td>214.4</td>
<td>12.4</td>
<td>18.2</td>
</tr>
<tr>
<td>Vaal 3</td>
<td>Quartzite</td>
<td>2.58</td>
<td>0.1550</td>
<td>0.2300</td>
<td>231.5</td>
<td>13.2</td>
<td>19.6</td>
</tr>
<tr>
<td>Vaal 4</td>
<td>Quartzite</td>
<td>1.21</td>
<td>0.0473</td>
<td>0.1010</td>
<td>483.3</td>
<td>17.1</td>
<td>36.5</td>
</tr>
<tr>
<td>Vaal 5</td>
<td>Quartzite</td>
<td>3.07</td>
<td>0.2140</td>
<td>0.2920</td>
<td>196.3</td>
<td>13.1</td>
<td>17.9</td>
</tr>
<tr>
<td>Vaal 6</td>
<td>Quartzite</td>
<td>1.14</td>
<td>0.0410</td>
<td>0.0947</td>
<td>508.7</td>
<td>16.4</td>
<td>37.9</td>
</tr>
<tr>
<td>Vaal 7</td>
<td>Quartzite</td>
<td>1.21</td>
<td>0.0489</td>
<td>0.1020</td>
<td>484.5</td>
<td>17.8</td>
<td>36.9</td>
</tr>
<tr>
<td>Vaal 8</td>
<td>Quartzite</td>
<td>3.08</td>
<td>0.2300</td>
<td>0.3050</td>
<td>195.5</td>
<td>14.0</td>
<td>18.5</td>
</tr>
<tr>
<td>Vaal 9</td>
<td>Granitoid</td>
<td>2.03</td>
<td>0.1030</td>
<td>0.1720</td>
<td>288.6</td>
<td>13.7</td>
<td>22.9</td>
</tr>
</tbody>
</table>
4.1. Apparent erosion Rates

Independent of the way the samples plot on Figure 4.1., four sample classes can be defined based on rock types and localities relative to the river. These classes, with ranges, average values and standard deviations of the apparent erosion rates are listed in Table 4.4. Although all ranges and standard deviations overlap, the average apparent value for the six quartzites sampled on ridges (and on old strath terraces) and pedestals along the river bed is much lower than that for the two quartzites sampled in the actual river bed, which give identical results showing the highest erosion rate of the four classes. This is fully in accord with the differences and ranges of cosmogenic nuclide concentrations shown in Table 4.3 above. For all classes of samples, the ranges and standard deviations of results are much greater than the uncertainties for the individual samples, thus demonstrating significant variation within sample classes. The observation that the quartzites are on average eroding at a relatively slower rate than the granitoid samples makes geological sense as they are more resistant to weathering and weathering promotes erosion.

Table 4.4.: Ranges and average apparent erosion rates of the samples, grouped into four classes.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Range of Erosion Rates (m/Ma)</th>
<th>Average Erosion Rates ± 1 SD (m/Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Quartzites (N=8)</td>
<td>0.81 (± 0.03) – 3.08 (± 0.23)</td>
<td>1.99 (± 0.98)</td>
</tr>
<tr>
<td>Ridge &amp; Pedestal Quartzites (N=6)</td>
<td>0.81 (± 0.03) – 2.79 (± 0.17)</td>
<td>1.62 (± 0.84)</td>
</tr>
<tr>
<td>River Bed Quartzites (N=2)</td>
<td>3.07 (± 0.21) – 3.08 (± 0.23)</td>
<td>3.08 (± 0.01)</td>
</tr>
</tbody>
</table>
Granitoids (N= 6) | 1.58 (± 0.07) – 3.68 (± 0.29) | 2.45 (± 0.89)

4.2. Apparent surface exposure ages
Sample Vaal 1 has the highest surface exposure age. Samples Vaal 2 and Vaal 3 have similar surface exposure ages with Vaal 4 showing the second highest exposure age of the ridge quartzites. Of the river bed quartzite samples, Vaal 5 and Vaal have very similar surface exposure ages, with Vaal 6 and Vaal 7 with the highest and second surface exposure ages respectively.

The granitoids have variable apparent surface exposure ages that can be considered in pairs. Samples Vaal 9 and Vaal 13 show similar surface exposure ages and Vaal 10 and Vaal 11 have similar surface exposure ages. Vaal 10 and Vaal 11 have the higher surface exposure ages with Vaal 14 and Vaal 12 showing the lower surface exposure ages respectively.

Table 4.5: Ranges and average apparent surface exposure ages of the samples, grouped into four classes.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Range of Surface Exposure Ages (kyr)</th>
<th>Average Surface Exposure Ages (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Quartzites (N=8)</td>
<td>195.5 (± 18.5) – 714.4 (± 54.6)</td>
<td>378.6 (± 25.4)</td>
</tr>
<tr>
<td>Ridge &amp; Pedestal Quartzites (N=6)</td>
<td>214.4 (± 18.2) – 714.4 (± 54.6)</td>
<td>433.6 (± 34.0)</td>
</tr>
<tr>
<td>River Bed Quartzites (N=2)</td>
<td>195.5 (± 18.5) – 196.3 (± 17.9)</td>
<td>196.0 (± 18.2)</td>
</tr>
<tr>
<td>Granitoids (N= 6)</td>
<td>170.3 (± 16.6) – 369.4 (± 28.1)</td>
<td>267.5 (± 22.3)</td>
</tr>
</tbody>
</table>

Four sample classes can be defined based on rock types and localities relative to the river. These classes, with ranges and the average values of the apparent surface exposure ages are listed in Table 4.5. above.
CHAPTER 5: DISCUSSION

In this chapter, the results as reported in Chapter 4 are discussed. I will consider the comparable apparent erosion rates and the apparent exposure ages, and will refer to the steady erosion vs constant exposure curves to discuss the results. The chapter will also consider the effects of the lithology, structural geology and the variable flow and gradients within the river bed as contributors towards the erosion rates that have been determined by the study.

5.1 Quartzites

It was observed (Chapter 3.1.2) that for the quartzite samples, there are a set of samples that can be interpreted as representing strath terraces based on where they were sampled. It can therefore be assumed that these surfaces have not undergone local erosion since the time they formed part of the river bed. In order to obtain realistic apparent surface exposure ages for these terraces, the average $^{10}\text{Be}$ concentrations of the samples with the lowest (similar) concentrations, i.e. those obtained on samples that currently experience erosion in the river bed itself (Vaal 5 and Vaal 8), were averaged and subtracted from the concentration values for the samples from the palaeo-strath terraces. This entails the assumption that samples Vaal 1, 4, 6 and 7 did not experience any erosion since the river was incised below their current level and therefore, apparent surface exposure ages for these samples are considered and recalculated (Table 5.1). These are shown below.

Table 5.1: Recalculated $^{10}\text{Be}$ concentrations and resultant surface exposure ages* for strath terrace quartzites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Lithology</th>
<th>$^{10}\text{Be}$ (atoms/g)</th>
<th>$^{10}\text{Be}$ (atoms/g)</th>
<th>Surface exposure ages (kyr)*</th>
<th>Internal uncertainty (kyr)*</th>
<th>External uncertainty (kyr)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaal 01</td>
<td>Quartzite</td>
<td>3.78E+06</td>
<td>2.48E+04</td>
<td>455.8</td>
<td>3.4</td>
<td>30.4</td>
</tr>
<tr>
<td>Vaal 04</td>
<td>Quartzite</td>
<td>1.97E+06</td>
<td>1.08E+04</td>
<td>233.9</td>
<td>1.4</td>
<td>14.7</td>
</tr>
<tr>
<td>Vaal 06</td>
<td>Quartzite</td>
<td>2.24E+06</td>
<td>7.32E+03</td>
<td>263.1</td>
<td>0.9</td>
<td>16.6</td>
</tr>
<tr>
<td>Vaal 07</td>
<td>Quartzite</td>
<td>1.97E+06</td>
<td>1.50E+04</td>
<td>234.4</td>
<td>1.9</td>
<td>14.8</td>
</tr>
</tbody>
</table>

*Minimum surface exposure ages calculated assuming rock density of 2.65g.cm$^{-3}$ and zero erosion. Calculated with the CRONUS-Earth Online Calculator (Balco et al., 2008) version 3 using the LSDn scaling scheme (hess.ess.washington.edu).

Among the ridge quartzite samples are also some (Vaal 2 and Vaal 3) that appear to portray relatively high “erosion rates”. This can be understood from the way such ridges erode: to a large
extent by mechanical erosion (i.e. rock falls), which from time to time exposes new surfaces that then have low cosmogenic nuclide concentrations to start with that have the potential to accumulate over time, until such a time where the rock breaks again. The rugged texture (Figure 3.4 and 3.6) observed on the ridge also supports the eroding mechanism that is suggested.

The texture observed on Vaal 5 and Vaal 8 was described as smooth (Figures 3.7A and 3.7C), also based on the sampling location. The polished surface is a result of the active fluvial action that the bedrock is exposed to continuously. The potholing observed near both the sampling points of these samples is proposed to be a result of the river carrying with it pebbles that get wedged into fractures and the continuous flow of the river making a small hole into the bedrock that continues to grow as the pebble grinds into the bedrock over time. The generally faster rates of erosion observed for these samples can be attributed to the fluvial action of the river. The river could also be carrying with it some sediment that, by friction and therefore abrasion, could be contributing to the lower cosmogenic nuclide concentrations observed.

The quartzites sampled on the ridge have been at surface for a very long time (they plot on the constant exposure curve (Figure 4.1) and have long surface exposure times, whether corrected or uncorrected) and therefore weathering has taken its toll on them. Although generally resistant to erosion, quartzite weathers when it has been at surface several 100,000 years by mechanical breaking of the rock as is seen on the ridge. The quartzites in the river bed present fresh surfaces because they are being eroded at present, even if the erosion is slow.

The recalculated apparent surface exposure ages of the palaeo-strath terrace range from 234 kyr to 456 kyr which are represented by both Vaal 4 and Vaal 7 and Vaal 1. The average corrected apparent surface exposure age is 297 kyr. Samples Vaal 4, Vaal 6 and Vaal 7 have relatively similar apparent surface exposure ages and accompanying uncertainties. These can be explained by the topography observed at their sampling locations (Figures 3.4 and 3.5). Based on these strath terrace exposure ages, we can attempt to determine the rate at which the river has been cutting into the ridge over time. The difference in elevation (Figure 3.5) between the highest of the quartzite samples (Vaal 1) and the closest river bed quartzite sample that is considered to be currently experiencing fluvial erosion (Vaal 5) is 42 m. This means that the river would have cut down 42 m in 456 kyr (the corrected apparent exposure age), which yields a very high cutting-in rate of 91 m/Ma. The same interpretation means that from the lowest of the ridge quartzites (Vaal 4) to the
current river level (Vaal 5) results in 62 m/Ma at an elevation difference of 5 m, for Vaal 6 – Vaal 5 it gives 19 m/Ma and for Vaal 7 – Vaal 5 it gives 17 m/Ma. The incision rates for uncorrected apparent exposure ages are about 60% of these values, but still very much higher than the erosion rates determined on the river bed samples. This serious contradiction is discussed further below.

5.2. Granitoids

Proximity to the river level appears to play a significant role in the understanding of the isotopic concentrations and therefore the erosion rates and surface exposure ages of the granitoid rocks (Figure 3.9). The granitoid samples will be discussed in order of their proximity to the current river channel.

Based on their sampling locations and the elevation of the samples above the present river bed, samples Vaal 9, 12 and 14 are essentially those that can be considered as experiencing (or recently having experienced) fluvial erosion. This can be seen from their apparent erosion rates that are relatively higher when compared to the other granitoid samples. These apparent erosion rates could be considered as the real erosion rates for the granitoid samples in these localities. This may vary as the river is anabranching in this area. The smooth texture observed from the sampling locations suggest that there is active erosion here. I would expect Vaal 13 to be considered with these since its apparent erosion rate is comparable, however, based on where it was sampled on what looks to be the top of a relatively solid boulder which has not had as much fluvial action (Figure 3.10E), this cannot be as easily deduced for the sample.

Vaal 10 experiences a different type of denudation, associated with weathering, which also explains its crumbly texture and very low erosion rate (the lowest of the granitoids). The sample shows little to no traces of fluvial action from the river and its history could therefore have a larger surface exposure component, similar to that of the ridge quartzite samples. However, due to the difference in the lithology and the typical weathering pattern of granitoid, the sample behaves differently. This can also be seen from the crumbly texture of the sample during sample preparation. As a result, it can be suggested that the sample be considered more for apparent surface exposure age determination. This can be supported by the sample’s distance from the current river channel. Although not as significant as the elevation factor found for the quartzite samples (although the sample is one of the two highest of the granitoid samples), the distance plays a role.
Vaal 11, like Vaal 10, is at quite a considerable distance from the river. However, the somewhat polished surface of the sample and of other rock surfaces at the sampling site suggests that there has been fluvial action in the (geologically speaking) recent past. The texture that is observed on the sample suggests that the sample has had more of the river input than Vaal 10. This sample can be considered an anomaly of the sampled granitoids. It is far enough from the present river bed and sufficiently elevated to not experience any current fluvial input, but not distant enough to experience the same weathering effects as Vaal 10. It is suggested that this sample experienced both erosion and exposure. This could mean that the resultant apparent erosion rate could be the minimum erosion rate and the resultant apparent exposure ages the maximum surface exposure age. This is also supported by where the sample plots on the steady erosion vs constant exposure curve (Figure 4.1). The results on this sample are in accord with the hypothesis changes in the river’s anabranching over time.

Vaal 13, although close to the current river bed and showing a polished surface, is elevated 1.5 m above the present river level. Similar to Vaal 11, it is uncertain what component of the $^{10}$Be budget can be ascribed to constant exposure. However, assuming its apparent exposure age of 268 ka as a maximum, its elevation of 1.5 m above the river bed would (in a calculation similar to that applied to the ridge and pedestal quartzite samples, see above), yield a maximum erosion rate of 5.6 m/Ma within the river.

5.3. Comparison of erosion rates and the conundrum of palaeo-strath terraces

When we consider the average erosion rates between the two lithologies, it can be seen that the granitoid rocks on average are eroding faster than the average quartzite rocks. However, we have to consider then that a true representation of the erosion rates between the two lithologies would be taking into consideration the average of the river bed samples for both the granitoid and quartzite samples. Table 5.2 shows the summarised erosion rates of the comparable quartzite and granitoid samples. The erosion rates between the granitoid and quartzite samples are identical well within uncertainties of the granitoid values.

It had been expected that the granitoids would erode faster than the quartzites due to the difference in their lithologies, and the quartzites indeed appear to be eroding on average more slowly than the granitoids (Table 4.4). Among the quartzites, however, there are large differences, which relate to where they were sampled. The observation that the two quartzite samples taken in the river bed
have identically high erosion rates to the river bed granitoids presents an apparent contradiction. This can be reconciled when considering the fact that the river is narrow where it breaks through the quartzite ridge and has clearly remained in the same channel for a long period. In contrast, anabranching in the granitoid region appears to have utilized different channels over time, as suggested by the data on sample Vaal 11. Further, the erosion rate in the river itself where it forms the canyon in the quartzite ridge cannot be slower than the lowering of the surface in the granitoid plain, otherwise there would be a lake within the central part of the dome.

Table 5.2: Summarised corrected erosion rates.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Average Erosion Rates ± 1 SD (m/Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River Bed Quartzites (N=2)</td>
<td>3.08 (± 0.01)</td>
</tr>
<tr>
<td>River Bed Granitoids (N= 3)</td>
<td>3.05 (± 0.22)</td>
</tr>
</tbody>
</table>

The apparent exposure ages for those samples that are not currently undergoing erosion in the river bed are summarized in Table 5.3. Here we can also see that on average, the quartzite samples have been exposed for longer than the granitoid samples, and the difference is significant outside 1 standard deviation.

Table 5.3: Summarised (uncorrected) apparent exposure ages for samples elevated above the current river bed.

<table>
<thead>
<tr>
<th>Sample ID and Type</th>
<th>Apparent Exposure Ages (kyr)</th>
<th>Average Exposure Ages (kyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaal 1 (Quartzite)</td>
<td>714.4 (± 54.6)</td>
<td>547.7 (± 41.5)</td>
</tr>
<tr>
<td>Vaal 4 (Quartzite)</td>
<td>483.3 (± 36.5)</td>
<td></td>
</tr>
<tr>
<td>Vaal 6 (Quartzite)</td>
<td>508.7 (± 37.9)</td>
<td></td>
</tr>
<tr>
<td>Vaal 7 (Quartzite)</td>
<td>484.5 (± 36.9)</td>
<td></td>
</tr>
<tr>
<td>Vaal 10 (Granitoid)</td>
<td>369.4 (± 28.1)</td>
<td></td>
</tr>
<tr>
<td>Vaal 11 (Granitoid)</td>
<td>328.2 (± 25.6)</td>
<td></td>
</tr>
<tr>
<td>Vaal 13 (Granitoid)</td>
<td>267.8 (± 23.0)</td>
<td></td>
</tr>
</tbody>
</table>
As shown above, the erosion rates measured in river beds appear to have a sound basis, being identical in the granitoids and the quartzites. However, the contradiction presented by the very much higher incision rates derived from the apparent exposure ages of elevated palaeo-strath surfaces in the quartzites needs to be addressed. Two hypotheses present themselves: (1) the erosion by the river in the quartzites did not occur at a steady rate but included catastrophic events. (2) the elevated palaeo-strath terraces are much older than the exposure ages suggest, and these exposure ages merely reflect the time when the sampled surfaces were uncovered, for instance by falls of overlying rock.

Hypothesis (1) is unlikely for two reasons. First, one can consider the “memory” of erosion rates. This is estimated from the erosion rates themselves and the depth at which the penetration by neutrons becomes negligible (in this first order estimation and for slow erosion, muons need not be considered). In the quartzite or granitoids alike, this depth is roughly 3 metres. For an erosion rate of c. 3 m/Ma as shown by the river samples, the memory is therefore estimated at about 1 Ma, broadly indicating steady erosion over that period of time in the river. This is much longer than the exposure ages calculated for the quartzites on the ridge, whether corrected or uncorrected. Second, if the river was at the level of sample Vaal 1 at the time indicated by the exposure age (corrected or uncorrected), then the dome area would have been covered by a lake, for which there is no evidence at all.

Hypothesis (2) is in accord with the way the quartzite ridges are seen to be eroded: by discrete events in which large rock masses fall down and are then made smaller by further weathering. Structural geology in the area can play a significant role in the way this mass wastage occurs. The Vredefort dome, having experienced the effects of the meteorite impact can be considered to be highly faulted and fractured. Considering that the impact event occurred over two billion years ago, this could have allowed the faulting and fracturing to develop further and contribute towards large rock falls. The implication is thus that the elevated surfaces considered palaeo-strath terraces were uncovered by such events at approximately the time indicated by the uncorrected exposure ages.

As a final thought, while the present erosion rates in the river may have remained steady for about a million years as discussed above, rates of precipitation in Southern Africa are documented to have decreased in the last 2 to 3 Ma (Bobe and Behrensmeyer, 2004), and a record stretching back
to 5 Ma for east and northeast Africa shows a steady secular drying up of the climate there over
the last 5 Ma (deMenocal, 2004; Feakins et al., 2005). It is therefore likely that the rate of river-
related erosion in the study area several million years ago was higher than it has been in the last
million-year period.
CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1. CONCLUSION

From the investigative study conducted, preparation of the samples of the two rocks types of interest, quartzites and granitoids, was carried out successfully using the methods adopted from the University of Vermont’s cosmolab. Extraction of $^{10}\text{Be}$ and $^{26}\text{Al}$ from these samples was carried out at that locality, after which the $^{10}\text{Be}/^{9}\text{Be}$ and $^{26}\text{Al}/^{27}\text{Al}$ ratios were successfully determined at iThemba Labs, Johannesburg. Concentrations of $^{10}\text{Be}$ and $^{26}\text{Al}$, and therefore erosion rates and subsequent exposure ages, were determined from these values.

For samples of the two lithologies of interest taken in the river bed itself, the erosion rates determined were identical within uncertainty levels at between 3 and 3.1 m/Ma. For quartzite samples taken on ridges, the data mostly yielded apparent exposure ages rather than erosion rates, as shown by their position relative to the curves of steady erosion and constant exposure in the $^{26}\text{Al}/^{10}\text{Be}$ vs $[^{10}\text{Be}]$ plot. These apparent exposure ages range from approximately 483 to 714 kyr. For granitoid samples taken at some distance from the river, it is mostly unclear what fractions of the $^{10}\text{Be}$ and $^{26}\text{Al}$ amount document steady erosion and constant exposure, respectively. Thus, if interpreted as exposure ages, these data yield maximum values and these are on average significantly younger than those of the quartzite samples taken at a distance from the river (330.8 kyr compared to 547.7 kyr respectively).

It is considered that although the two groups of samples were different, and erosion was driven by different factors (lithology and proximity to the river channel) the similarity of the erosion rates determined for samples from the river bed itself is due to the river channel in the quartzites being narrower and constantly in one place, while in the granitoid terrain, the river is anabranching. This apparent “equilibrium” explains the absence of a lake in the central part of the dome and continuous in and out flow of the river through the dome.

6.2. RECOMMENDATIONS

I recommend further studying towards understanding the river by studying the lithologies that are outside the anabranching area of the river and determining whether the erosion rates in the dome are comparable. This can contribute towards building more erosion rate data for the region and also towards understanding the river’s influence on the evolution of the landscape in the area.
The Vaal river has been noted to be experiencing a substantial amount of pollution and although minimal on a larger geological scale, perhaps consideration towards the contents of the water that flows through the dome could also be investigated by another study to determine if this could affect the rate at which the bedrock in the area is being eroded.

Extensive investigations in this regard could contribute towards understanding the evolution of the area and potentially could help us understand better the behaviour of the rocks in the dome other properties that could be driving the erosion rates in the area.
REFERENCES

Adolfsson, M. 2014. Visualising the volcanic history of the Kaapvaal Craton using ArcGIS. Dissertations in Geology at Lund University. Department of Geology, Lund University.


Balco, G. 2006. Converting Al and Be isotope ratio measurements to nuclide concentrations in quartz. Cosmogenic Nuclide Lab, University of Washington.


Dirks, P.H.G.M., Placzek, C.J., Fink, D., Dosseto, A. and Roberts, E. 2016. Using 10Be cosmogenic isotopes to estimate erosion rates and landscape changes during Plio-
Pleistocene in the Cradle of Humankind, South Africa. *Journal of Human Evolution*, 96. 19-34.


APPENDICES
The following are sample processing protocols have been designed to yield sample of the correct grain-size for processing in the mineral separation laboratory.

A: PHYSICAL SAMPLE PREPARATION
   (i) Crushing and sieving of bedrock samples

B: CHEMICAL SAMPLE PREPARATION
   (i) Leaching and etching
   (ii) Density separation
   (iii) Froth floatation

C: QUARTZ PURITY CHECK AND ICP RESULTS
   (i) QUARTZ PURITY CHECK
   (ii) ICP RESULTS

D: COLUMN CHROMATOGRAPHY

E: AMS RESULTS

F: CRONUS-EARTH ONLINE CALCULATOR RESULTS
A: PHYSICAL SAMPLE PREPARATION

(i) Crushing and sieving of bedrock sample

Objectives

1. Reduce the bedrock samples by breaking them into small pieces.
2. Crush and grind rock to the appropriate grain-size fraction.
3. Sieve samples to the appropriate grain-size fraction (250-710 microns).

Materials and equipment

- Manual crusher for breaking up rock
- Rock or sledge hammer
- Plastic sample bags and markers
- Jaw crusher
- Pulveriser (plate grinder)
- Sieves
- Sieve shaker
- Eye protection
- Hearing protection
- Particulate mask (respirator)
- Lab coat
- Ultrasonic bath
- Hotdog roller
- Carbonator

Procedure

Entering samples in the database

1. Each sample needs to be entered in the database before it is processed. Data entry is usually done by the person who collected the sample and includes:
   - Sample ID,
   - Sample site photographs,
• Sample information including rock type,
• Collector, and
• GPS location (co-ordinates)
• Scanned field notes and sample sheets also need to be uploaded.

**Initial sample preparation** – To maintain sample integrity and avoid confusion between samples, it is imperative that you work with only one sample at a time.

**NOTE:** Whenever you are working with the rock cutter, jaw crusher, and the plate grinder, safety glasses or goggles, as well as hearing and respiratory protection are mandatory.

**For Bedrock Samples** –

• Wire brush sample to remove lichen and adhered material.
• To avoid contaminating samples with foreign rocks or pieces of rock from other samples, make sure to clean the manual crusher with a vacuum before adding samples. Work in an area free of other rock material. Sweep and vacuum between samples.
• Place rock samples into the rock cutter and break the sample into small fragments.
• Place rock fragments into a plastic sample bag and label the bag with the sample name.

**Jaw Crusher**

• The crusher is turned on by first making sure the power switch in on and then pulling out the red kill button.
• First, check that the crusher has been cleaned. If not, clean by vacuuming. If this is your first rock to crush, blow out the crusher with compressed air. Run it for 10 seconds and blow it out again. Vacuum up any stray bits of rock.
• Rock and clast samples must first be crushed using the steel mortar and pestle so that fragments are small enough to fit in the jaw crusher.
• Pieces are then jaw crushed.
• Make sure there is a pan under the jaw crusher to catch falling pieces of rock.
• Only after the jaw crusher is running, should material be fed into the feed chute. If the machine jams, immediately hit the red kill button and pull the power lever to the off position BEFORE clearing the jam by removing the safety shield.

**IMPORTANT:** Never operate the crusher without the safety shield in place and never place a rock in the crusher when it is not running. These actions can be dangerous as rocks could be ejected suddenly and the machine can be broken if rocks are placed between the jaws without the machine running. ALWAYS push in the off button and pull the power lever to off before cleaning or servicing the machine.

• After each use, remove the safety shield, vacuum all parts of the crusher paying special attention to the area below and behind, and only then blow out the crusher with compressed air, followed by vacuuming up any rock fragments.

**Pulveriser (Plate grinder)**

• After jaw crushing, the now smaller fragments are fed into the plate grinder.
• Before grinding any samples, clean the plate grinder. Do this by throwing the power lever to off then by opening the plate compartment, separating the plates, vacuuming all areas, and only then blowing out the machine thoroughly with compressed air. Make sure to clean completely the compartment where the sample tray resides. Use the vacuum to remove all loose rock and dust liberated by the compressed air.
• Turn the plate grinder on by setting the time and pulling out the red knob.
• Make sure the large wooden door is closed to contain as much dust as possible. Run the plate grinder with the door closed.
• Add the crushed sample fragments into the grinder in between the plates and close the pot.
• You should grind and sieve a small amount of sample through and discard it to clean and pre-contaminate the plate grinder and to check that the bulk of the sample is in the 250 to 710 micron size fraction.
• To avoid injury, keep your hands and fingers away from all moving parts until the machine has stopped
• When you are finished grinding a sample, push the kill button in, throw the power supply lever to off, and clean the grinder completely between every sample and at the end of the day. Vacuum first and then use compressed air followed by a second vacuuming.

Sieving

• Use the stainless 250 and 710 micron sieves and always clean them again before use. Place a pan at the bottom of the stack, then the 250 micron sieve, then in order of increasing size until the 850 micron sieve, then the filler stack.
• Fill the 1mm sieve about 2/3 full. Place the filler sieves on top and then a lid on top of the stack.
• Place the stack on the shaker and run for one minute. Remove the filler sieves and separate the 710 and 250 micron sieves carefully to avoid spilling.
• Pour the sample once again through the sieves and onto the sieve shaker. Start the shaker until the sample has gone through the sieves.
• Place the sample in two labelled bags with the fraction range required and the smaller fraction in the other. Place these bags in a larger bag labelled with the sample name.
• The bags should have sample name and grain size written with a marker on the outside.
• Clean sieves between each sample using the small wire brushes stored in our locked drawers. Don’t worry that a few grains are left jammed in the sieves. They won’t come out.
• When you have completed sieving, vacuum the closet in which the sieve shaker resides and place the sieves back in the locked drawers.
• The samples should be rinsed in order to remove residual dust after sieving.

B: CHEMICAL SAMPLE PREPARATION

(i) LEACHING AND ETCHING

Material:

• Rinsed and dried samples
• Sample bottles
• HCl mixed solution (1:1)
• HF//HNO₃ mixed solution (1:2)
- Ultrasonic bath
- Hotdog roller
- Milli-Q water

Procedure 1:

- Pour the rinsed sample into sample preparation bottles.
- Add the HCl solution to cover the sample in the bottles and place the bottles in the ultrasonic bath for 24 hours.
- After 24 hours, decant the straw-coloured solution into the appropriate waste container and rinse the sample once.
- Repeat the process for another 24 hours and rinse the sample three to five times.
- Dry the samples overnight.

Procedure 2:

- Add the HF/HNO₃ solution to cover the sample filled bottles.
- Place the samples in the ultrasonic bath for 24 hours.
- After 24 hours, decant the milky solution in the appropriate waste container and rinse the sample once.
- Pour the HF/HNO₃ solution into the bottles again and place onto the heated hotdog roller for 24 hours (Ensure that the drip tray is placed under the roller to avoid any leakage disasters).
- After 24 hours, decant the milky solution into the appropriate waste container and rinse the sample again.
- After the second 24 hours, add the HF/HNO₃ again and place the bottles into the ultrasonic bath for another 24 hours.
- After the 24 hours has lapsed, decant the solution and rinse the sample five to eight times.
- Dry the samples overnight in preparation for the density separation process.

(ii) **DENSITY SEPARATION**

Material:
• Leached and etched dried samples
• Separation funnel
• Mixing rod
• Filter and filter paper
• LST density separating liquid (± 2.85 g/cm³)
• Milli-Q water to dilute the LST

Procedure:

• Set up the apparatus for the separation process and test the suction power by pouring a little Milli-Q water through the system.
• Prepare the density liquid by adding small volumes (1ml at a time) into the LST separating liquid.
• Test the density by using the hydrometer. (The ideal density is 2.76 g/cm³)
• Add the density separation solution into the separating funnel and pour the dried sample.
• Stir the sample into the liquid with the rod and give it time to settle.
• The heavier minerals should have sunk down to the bottom with the lighter mineral floating.
• In between, the separating liquid should be dividing the minerals.
• Open the separating funnel tap to remove the heavy minerals and close the tap just after.
• Decant the filtered heavy minerals appropriately.
• Open the tap to collect the lighter minerals.
• Rinse the samples with the Milli-Q water and dry the samples in preparation for the froth floatation process to follow.
• Do this for each sample
• Clean the apparatus after every sample is separated.

(iii) FROTH FLOATATION
The purpose of this process is to separate feldspar and mica from quartz.

Material:
- Rinsed sample
- Soda carbonator
- Acetic acid
- Lauryl amine
- Hydrofluoric acid
- Eucalyptus oil
- Salad bowl

Procedure:

- The frothing technique is done with a soda carbonator and a mixture of 1ml/L acetic acid and 1 g/L lauryl amine in 1 L pure water. The lauryl amine dissolves better in the acetic acid and keeps the pH at ~5. This solution is then mixed with 10 L water and then carbonated.
- The quartz must be pre-treated for 1 hour with a 1% solution of hydrofluoric acid (HF). This HF solution changes the surface chemistry of the feldspar/mica and quartz grains making the feldspar/mica hydrophobic and the quartz hydrophilic.
- After an hour, decant the 1% HF solution, and without rinsing or drying the sample, pour it into a large salad bowl.
- Add a few drops of pure eucalyptus oil to the mixture and then the carbonated solution. The eucalyptus oil will hold the bubbles together and it will form a head (like on top of a beer) where the feldspar/mica will be.
- Wait a few seconds to let the solution of carbonated minerals settle. Then pour off the feldspar/mica and what is left will be quartz and other heavy minerals. This can be repeated if necessary.
- Decant the quartz-rich and feldspar-rich fractions into separate labelled drying dishes and dry in the oven.

(iv) FINAL ETCH

Material:

- Rinsed and dried samples
- Sample bottles
• HCl mixed solution (1:1)
• HF//HNO₃ mixed solution (1:2)
• Ultrasonic bath
• Shaker
• Milli-Q water

Procedure:

• Add the HF/HNO₃ solution to cover the sample filled bottles.
• Place the samples in the ultrasonic bath for 72 hours.
• After 72 hours, decant the milky solution in the appropriate waste container and rinse the sample once.
• Pour the HF/HNO₃ solution into the bottles again and place onto the shaker for one week.
• After the week hours, decant the milky solution into the appropriate waster container and rinse the sample five to eight times.
• Dry the samples overnight in preparation for the purity check.

C: QUARTZ PURITY CHECK AND ICP RESULTS

(i) QUARTZ PURITY CHECK

Material:

• Pure quartz samples in a vial
• Prepared ICP-OES standards
• Savillex® Teflon beakers
• Hotplate
• Acid mask
• Ultrapure Hydrofluoric Acid (HF)
• Nitric Acid
• Milli-Q water
• Centrifuge tubes (15ml)
• Pipettes
Purity check for cosmogenic nuclide samples before dissolution – read carefully and plan before starting

The purpose of this purity check is to see if cleaning of the samples has been successful to produce a sample close to pure quartz. We need to confirm the removal of meteoric beryllium (\(^{10}\)Be) and the other undesired minerals such as k-feldspar and micas (for Al and Fe). It applies to samples that have been subjected to heavy liquid density separation and froth flotation and/or magnetic separation in most cases, HCl leaching and the HF-HNO\(_3\) etching steps. If a sample still contains dark and reddish grains, which are clearly not quartz, then it is not ready for this purity check.

Procedure (to be done gravimetrically):

- Homogenize the sample and take \(~ 5\) g aliquot with a vial
- Weigh clean Savillex® beaker, followed by weighing in \(~ 0.1\) g of sample (add a little bit of water after noting the weight of the sample),
- Add 1 mL HNO\(_3\) concentrated first and then 2 mL HF concentrated
- Cap the beaker tightly and heat at 120-130 °C until all sample dissolves.
- When dissolution is complete, dry down the sample by opening the beakers. NB: Be is volatile and evaporates at high temperatures. So dry down at 60 °C (best to do it overnight)
- Add 1 mL 3M HNO\(_3\) while the beaker is still on the hotplate and dissolve the precipitate
- Cool down the solution and transfer to a suitable centrifuge tube.
- Centrifuge and pipette the solution into another tube/vial if there are solids at the bottom. Prepare solution for ICP-OES measurements – dilute to 10 mL to achieve less than 3 % HNO\(_3\) matrix.
- Analyse for Al, Be, Ca, Fe, K, Mg, Mn, Na, Si and Ti.
- Prepare standard solutions with Be at concentrations 0.1 ppm, 0.5 ppm, 1 ppm, 5 ppm, 10 ppm

See Table 1 below for ICP Results.
(ii) **ICP RESULTS**

Table 1: Summarised results from ICP-OES analysis

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample Type</th>
<th>Al Average (ppm)</th>
<th>Ca Average (ppm)</th>
<th>Fe Average (ppm)</th>
<th>K Average (ppm)</th>
<th>Mg Average (ppm)</th>
<th>Mn Average (ppm)</th>
<th>Na Average (ppm)</th>
<th>Ti Average (ppm)</th>
<th>Total Cations (ppm)</th>
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<tr>
<td>Vaal 1</td>
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<td>64</td>
<td>2</td>
<td>20</td>
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<td>1</td>
<td>92</td>
<td>192</td>
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<td>19</td>
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<td>106</td>
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</tbody>
</table>
D: COLUMN CHROMATOGRAPHY (UVM STEPS)

(i) SAMPLE DIGESTION

Weighing in quartz [about 1 hour] - This is a two-person job.

1. Turn on the balance and the anti-static device.
2. Use the weights to test balance and record the masses on the clipboard.
3. Select a batch of samples to dissolve. Place them together in a rack.
4. Use the blank rotation schedule pasted on the inner cover of the batch book to determine the position of your blank(s) and CRONUS standard material, then populate the other positions accordingly. Update the blank rotation schedule by adding your batch number on the appropriate line. If possible, order your samples in such a way that they make the most sense – alpha or numeric order will make them easier to keep track of overall.
5. On each quartz tube, place a small piece of lab tape on the lid with the batch number written on it
6. Open up the batch template on the lab computer in the corner (do this from cosmolab). Add the batch number for your new batch and save the batch sheet in the folder “in situ batches” to cosmolab using the main lab computer. Enter your samples on the batch sheet and update the date, batch number and carrier fields. THIS IS CRITICAL – makes sure all the information is there, specifically carrier name, double check.
7. In the “min test ICP data” page of the batch sheet Excel workbook, enter all cation concentration data from the quartz test results on the sample tube. Considering these impurities will prevent overloading of the cation and anion resins and thus prevent impure samples.
8. Take out a bin with 12 clean teflon bottles. PUT ON THIN NITRILE GLOVES. For low-level samples, label them with yellow tape. For high level samples, use blue tape. On the tape, put the batch number and sample position letter (A-L) and the sample name. Label the blank with the batch number and BLK. If there are two blanks, use BLKX for the second blank. Use two blanks for low-level samples. Place the labelled bottles in the bottle rack in A-L order.
9. Place the appropriate teflon/polycarbonate digestion block on the bottom shelf of the weigh-in cart and fill with sample bottles.
10. Place the sample rack on top shelf of the black cart with the antistatic device.
11. Take out the Al carrier pipette (variable 1 ml) and place a new tip on it and hang it on the labelled pipette stand. Place a wipe under the tip to catch any drips.
12. Decide on what Be carrier you will use. Add carrier type and name to the spreadsheet.
13. Bring over the carrier spill tray and sit it on the counter top. Take the appropriate Be carrier bottle and the taller Al carrier bottle and place them both in the spill tray on the counter next to the balance along with Be waste bottle.
14. Attach a 10 ml repipettor tip to the X-stream pipette. Load the pipette tip with sufficient low level Be carrier (the pipette will do this automatically). Discharge the first partial shot to waste in the Be waste bottle. Place a wipe under the tip to catch any drips.
15. One person should sit by the balance wearing gloves and goggles. The other person should sit by the computer wearing goggles.
16. Use check weight set to verify the performance of the balance and record each check weight result on the clipboard hanging on the wall behind the balance table.
17. Take out bottle A. To remove static from the bottle, wave it through the anti-static U-shaped upright for 5 seconds. MAKE SURE THE DEVICE IS ON. The green light should be glowing.
18. TARE the balance.
19. Then, mass the empty bottle with lid.
20. To record the mass on the batch sheet electronically, press the “piece of paper button” followed by the CF button on the balance. The person at the computer needs to highlight the cell where the data belong and hit Apple-V. It takes about 5 seconds for the data to transfer from balance to computer. Check the number by reading it back to the balance operator. Save the sheet after every data transfer.
21. Take the lid off and set aside.
22. TARE the balance with the empty bottle on it.
23. While the balance is taring, wave quartz tube through the anti-static U-shaped upright for 5 seconds.
24. Pour the quartz into the bottle adding no more than 45 grams (large bottle, low level samples) or 23 grams (small bottle, high level samples). If you add more quartz it will TAKE MUCH LONGER to digest. Record the mass on the batch sheet.

Keep total Al < 7500 ug by adjusting sample size and total load (minus Fe since it is removed by anion columns) below 10000 ug. Using more sample can overload the columns and result in loss of Be and loss of Be purity.

25. Calculate the amount of Al carrier needed to get to optimal Al total (LOOK AT THE BATCH SHEET FOR HELP, PRIME needs 1500 ug; LLNL needs 2500, SUERC can go to 3000 but less carrier means higher ratios). The batch sheet does this by multiplying the quartz mass times the Al-content of the sample from the ICP data printed on the tube (in ug/g or ppm) and subtracting that from 2250. If there is more than 2250 ug of Al natively in the sample, add no carrier. Add the extra Al using the adjustable 1 ml pipettor and the carrier. Record the mass on the batch sheet electronically.

26. TARE the balance. Add 250 ug of Be (as carrier) using the x-stream. Record the mass on the batch sheet electronically. Note that the mass of Be solution will vary depending on the concentration of carrier. Repeat this for all samples.

27. When it is time to load the blank, add NO QUARTZ but open the Al carrier bottle. And add 2250 ug of SPEX 1000 ppm Al carrier (2 ml). Close the carrier bottle.

28. TARE the balance. Add 250 ug of Be carrier this is about 0.5 ml beryl carrier for low level samples, the exact value will change depending on the carrier concentration). Record the mass on the batch sheet electronically. Save the sheet. Make sure to note the carrier you are using on the batch sheet.

29. Remove bottle from balance and place it in the digestion rack.

30. Grab the next bottle. Repeat above process.

31. Place each bottle as it is filled with sample and carrier into the digestion rack.

32. Repeat until all 12 samples are loaded.

33. Save and print the batch sheet and attach it to a clipboard. Place the appropriate colour tape (yellow or blue) across the top and write your name and the batch number on the tape.

34. Clean up by vacuuming the balance chamber to remove all quartz, putting away carrier, disposing of Be tip as Be waste and Al tip in trash.
Table 2: Compiled lab sample digestion data

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Position</th>
<th>Batch Number</th>
<th>Sample Mass Added (g)</th>
<th>Be Carrier Added (g)</th>
<th>Al Carrier Added (g)</th>
<th>Total Al Quantified by ICP-OES (ug)</th>
</tr>
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<tbody>
<tr>
<td>BLK</td>
<td>G</td>
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NOTE: 9Be was added through a carrier made at UVM with a concentration of 304 ug/mL; 27Al was added through commercial SPEX carrier with a concentration of 1000 ug/mL
Adding Acid to Quartz and Ramping Up Temperature for Digestion

1. Don all protective gear including double gloves, yellow rubber lab coat, and face shield over goggles.
2. Place a spill tray in the hood. Get out the teflon beaker used for HF decanting, take off the parafilm, and place the beaker in the hood in the spill tray.
3. Carry the digestion block to the hood and place it on the small hotplate.
4. Open bottle A. Using the Milli-Q wash bottle, saturate the sample with water so the quartz is well wetted.
5. Then, add HF to the sample decanting from the large (2.5 l) bottle to the graduated TEFLON beaker. WORK IN A SPILL TRAY. Use about 5 times the volume of HF to the mass of sample (for a 20 g sample, add 100 ml of HF; for a 40 g sample, add 200 ml of HF). Cap the sample and place it back on the digestion block. DO NOT SQUEEZE THE BOTTLE OR RISK MAKING AN HF SQUIRT GUN. (See Table 2 above)
6. Repeat for all samples from B-L.
7. Let the samples sit in acid for at least an hour with no heat. This allows very fine quartz to dissolve. When samples are digesting, DO NOTHING ELSE IN THE HOOD and make sure the SASH IS ALL THE WAY DOWN.
8. Over the course of several days, the goal is to ramp the samples up to an overnight digestion temperature of 130 to 140°C, hot enough to speed digestion, but cool enough to prevent boiling.

**IMPORTANT:** Note on the white board every time when the temperature was increased.

9. Bring the hotplate to 60°C and let the samples sit for at least 2 hours.
10. After an hour, if there is no reaction, raise the temperature by 10 degrees. Wait another hour and if there is no reaction, raise the temperature again, at most 10 degrees per hour. If at any point, the samples are boiling (more than slowly rising bubbles), turn down the heat and wait.

**For the first day, take the samples no higher than 90°C degrees; then let them sit overnight.**

**IMPORTANT:** The reaction that dissolves quartz is EXOTHERMIC and can run away causing boiling and venting of hot gas from the bottle top. Violent reaction will occur if you are impatient and ramp too quickly. The sensitive range is 80 to 115°C. If the samples boil, turn down the hotplate and stay OUT OF THE HOOD.
11. On the second day, continue ramping up the samples. Once samples are above 90 degrees, ramp them by no more than 5 degrees every few hours. If there is more than a bubble emitted per 30 seconds do not increase the temperature.

12. On the third day ramp the samples to their final temperature (see below). They should sit at final temperature over night to ensure complete dissolution.

13. For the large bottles bring the hot plate to 140°C (they boil at about 150°C); this will keep the samples just sub-boiling and quicken dissolution. Back down the temperature if you see any more than mild action.

14. For small bottles, bring the hotplate to 135°C (they boil at about 140°C); this will keep the samples just sub-boiling and quicken dissolution. Back down the temperature if you see any more than mild action.

15. Leave the samples heating until they are all fully dissolved, the liquids will be clear and there will be only a few bubbles on the bottom and sides. There will be no floating material.

16. Make sure that the samples cool for at least 2 hours until they are room temperature before aliquoting. It is very dangerous to handle warm HF.

**ICP Aliquot**

1. This is a dangerous job because you are handling large amounts of HF in open beakers. Make sure someone else is around. Work only with cold acid and when you are not tired.

**NOTE:** do not block the grills with objects in the hood or risk breathing HF.

2. **DO THIS ONLY IF YOU ARE ALERT. YOU ARE WORKING WITH UNLABELED BEAKERS. ORDER MATTERS. “ORDER MEANS EVERYTHING”**

3. **Bring out the following teflon ware: 12 evaporation beakers (180 ml for high level samples; 240 ml for low level samples, DO NOT LABEL THE BEAKERS WITH TAPE), 24 ICP aliquot beakers in their boxes. All should be dry and clean. Place the black cart next to the hood and place the two beaker boxes on the cart. Also place a clean beaker with 5 ml pipette tips (12) on the cart.**

4. **Arrange the beakers on the table top or in the cart in the same order they will go on the hotplate. Label the ICP beakers with letters from A-L AND THE BATCH # corresponding to the samples; note the dilution on each beaker.**
5. Make sure the large and small hotplates are in the digestion hood with beaker holders in place.
6. Place the CHEAP balance in the hood next to the large hotplate and level the balance. Place the pipette carousel in the hood.
7. Use check weight (2, 10, 100 g) set to verify the performance of the balance and record each check weight result on the clipboard hanging on the wall behind the balance table.
8. Put a few wipes on the grill and a DI squirt bottle in the hood for acid spills.
9. Place a “waste” beaker in the hood to hold used pipette tips (these will have trace amounts of HF and Be on them).
10. Place a clean tip on the 5 ml variable pipette.
11. **Once all bottles are ready, don the full safety gear including face mask and smock.** Double glove. Make sure there is no open skin showing between the gloves and the smock. Use gauntlets.

**NOTE:** ICP split rack goes on the small hotplate so the bottle rack needs to come off and sit on the hood deck. Do this transfer carefully since the bottles still contain some HF.

**NOTE:** Accurate weights require patience. Wait for vibration averaging to level out; snowflake will appear and remain in lower left of balance screen. Only then, take the balance reading.

12. Grab the evaporation and ICP beakers for the first sample. Place the lids in the respective boxes.
13. Place the ICP beakers (no lids) in the spill tray in the hood for the first sample.
14. Take the first sample out of the digestion block.
15. Carefully tip the bottle toward its side and roll to remove droplets from the lid. **DO NOT SQUEEZE!**
16. **MASS THE BOTTLE with LID ON and record.**
17. In a spill tray, pour the sample into its evaporation beaker. Leave any solids behind even if you need to leave an ml or two of liquid with the solids.
18. **DO NOT LABEL THE EVAPORATION BEAKER WITH TAPE – JUST PUT IT IN THE RIGHT POSITION FOR ITS LETTER.**
19. Put the 2 ml (4 ml for low level) split beaker for ICP on the scale and **TARE** and wait for TARE to stabilize.
20. Check that the 5 ml variable pipettor is set to 2 ml (4 ml for low level). Then draw up SLOWLY, 2 ml of acid (4 ml for low level) from the evaporation beaker and release it SLOWLY it into the ICP beaker.

21. MASS the solution in the ICP beaker with the 2 ml aliquot in it (4 ml for low level) and RECORD the mass. Put the beaker on the hotplate in its hole.

22. Put the 4 ml split beaker (8 ml for low level) for ICP on the balance.

23. TARE the 4 ml ICP beaker (8 ml for low level).

24. Check that the pipettor is set to 4 ml (2 shots of 4 ml for low level). Then draw up SLOWLY, 4 ml of acid (twice by 4 ml for low level) from the large beaker and squirt it into the ICP beaker. Repeat so there is about 4 ml of solution (8 ml for low level) in the second ICP beaker.

25. MASS the ICP beaker and RECORD the mass. Put the beaker on the hotplate in its proper hole.

26. Place the large beaker on the hotplate to dry off in its proper hole.

27. When done with a sample, place both the pipette tip in the dirty tip beaker, immersing it in water. Place the empty bottle back in the rack. Repeat for all.

28. Add 2 ml of HClO4 to each of the 12 large beakers containing samples. Do these additions using the repipettor and the dedicated repipette tip. Release the acid SLOWLY so as to prevent spatter and cross-talk between samples.

29. After you are done using the tip, rinse it in milli-Q water by filling the clean “acid only” beaker with milli-Q and filling/emptying to the sink, the reservoir, several times. Rinse the beaker out with mill-Q and dry in the oven. Once it is dry, add parafilm and replace the beaker on its shelf.

30. Then, use a repipettor and the 0.5 ml reservoir to add 25 ul (dial set to 2.5 whereupon the display should read 25 ul) of concentrated H2SO4 to each ICP aliquot. We add the H2SO4 so that when the ICP splits dry down, they stay in single drop of acid and do not dry off (and fly away in a fit of static). Release the acid SLOWLY so as to prevent spatter and cross-talk between samples.

31. Rinse out all the dissolution bottles in the wash hood with DI water to remove any undissolved material and HF.
32. If there is black material in or on the walls of the bottle, use a wipe and ethanol to remove the material. Be gentle, so as not to scratch the bottles. It may help to use a teflon stir stick wrapped in a wipe and soaked in ethanol to clean the deep recesses of the bottle.
33. Place the bottles and lids in a 4-litre jug and sonicate overnight with 1% nitric acid to clean.
34. Set the SMALL hotplate to 120 degrees C until the ICP aliquots are dry; then turn hotplate down to 60°C.
35. Set the LARGE hotplate to 150°C. When the samples in the LARGE beakers are nearly dry (only several ml remaining) set the hotplate to 230 and evaporate overnight.
36. In the wash hood, rinse off with 1% nitric, using the sprayer, from any and all materials used in the hood such as spill trays and pipette stands. Wash the digestion rack the same way, rinse very well, and dry on the counter.

**Bringing up ICP aliquots**

1. Make sure that the small hotplate and the samples on it are at 60°C. This could take an hour or two of cooling if they are hot.
2. Only bring up the aliquots after the initial Perchloric acid has dried off from the large beakers and NO FUMING is occurring.
3. USE 24 CHEAP UNWASHED PURPLE CAP TUBES ONLY for this step.
4. Place CHEAP balance in the hood and level and use check weight (2, 10, 100 g) set to verify the performance of the balance and record each check weight result on the clipboard hanging on the wall behind the balance table.
5. Pour about 125 ml of Ga/Y spiked 0.5% H2SO4 into a DRY clean acid beaker. This dilutant is stored in the white side cabinet in a 4 litre jug. Make SURE you have the RIGHT solution.
6. The dilutant should be added to the aliquots with a 5 ml variable pipettor.
7. One at a time, remove a beaker from the rack and tare.
8. Add 5 ml shot of Ga/Y spiked weak H2SO4. Record the mass on the batch sheet. CAP the beaker. TIGHTEN THE LID.
9. Repeat for all beakers.
10. LET THE BEAKERS SIT ON THE HOT PLATE AT 60 DEGREES FOR AT LEAST AN HOUR. Using less time could result in incomplete dissolution. Don’t leave samples overnight unless very tightly capped.

11. Once all samples are massed, remove the balance from the hood and replace with the vortexer.

12. RETIGHTEN EVERY LID. Place a wipe on the vortex foot, folded over several times. Vortex every sample twice, once right side up, once upside down. Each spin should last at least 5 seconds.

13. Transfer each sample to its labelled tube ALONG WITH THE TAPE LABEL FROM THE BEAKER. DON’T RINSE THE BEAKERS into the tubes.

14. As soon as you are done with a beaker and lid, drop it into a 1% Nitric acid cleaning bottle.

15. Wash the ICP beakers in 1% nitric overnight in the ultrasound.

16. Place the tubes in a 25 hole foam or purple plastic rack. Use a piece of tape to label over the top of the tubes in their rack with the words ALIQUOTS, BATCH-XXX.

17. Put the rack and tubes in the white acid storage cabinet.

Perchloric Drydowns

1. Bring out the repipettor, the pipette carousel, and the Perchloric tip. Place a spill tray in the hood and bring out the 240 ml Perchloric beaker. Also place the medium or large clean acid beaker in the hood. It will be used to hold the repipette tip while the dry down is happening. Make sure hotplate is set to 230.

2. Double glove and don the smock and the face shield. This is VERY important as you are adding Perchloric to hot samples.

3. Add 2 ml of Perchloric acid to each sample using the repipettor and aiming for the sides of the beaker to ensure the cake is wetted.

4. Release the tip into the empty clean acid beaker and LEAVE in the hood. LEAVE the pipette carousel in the hood.

5. REMOVE the pipettor and store it vertically on the wall mount. This is CRITICAL. Pipettors left in the hood and exposed to acid fumes will quickly become inoperable. Leave the acid in the hood with the cap on.
6. MAKE SURE THE SASH IS ALL THE WAY DOWN. Evaporate the Perchloric Acid until the white fuming totally stops (this will take between two and three hours).
7. REPEAT the process above one more time.
8. BEFORE going home for the evening, ADD 4 ml so that each sample is treated for a total of four Perchloric acid dry downs (including the co-evaporation with HF). SWITCH to 50ml reservoir to do this in order to avoid fumes.
9. After you are done using the repipettor tip, rinse it in milli-Q water by filling the clean “acid only” beaker with milli-Q and filling/emptying to the sink, the reservoir, several times. Rinse the beaker out with milli-Q and dry in the oven. Once it is dry, add parafilm and replace the beaker on its shelf.
10. At the end of the drydowns, run the hood washdown by turning the red handle and letting the water run for 30 seconds. This removes acid from the hood plenum and lower exhaust where most of the acid has condensed.

HCl Drydowns
1. USE full PROTECTIVE gear including double gloves because the rims of the beakers contain droplets of Perchloric Acid.
2. Turn hotplate down to 160 °C and wait until hotplate and samples have cooled to 160 °C.
3. Pull out 240 ml concentrated HCl jar and repipettor. Place a spill try in the hood. Place the 25 ml HCl tip on the repipettor and the pipette on the carousel in the hood. Place the clean acid beaker in the hood to hold the tip between shots. Fill the tip with HCl.
4. Gently add 2 ml concentrated HCl to each sample using the repipettor. Aim for the bottom edges of the beaker. Remove the pipettor from the hood and hang outside the hood leaving the tip in the clean acid beaker. Leave the carousel in the hood.
5. Use the mirror to check that each sample is in a puddle of HCl. If not, one at a time, pick up the sample, bring it to the front of the hood and swirl gently so as NOT TO SPLASH.
6. Heat the sample at 160 to drive off the HCl which usually takes about 90 minutes.
7. Repeat the process a second time. The repeated HCl drydowns ensure that the sample is in chloride form before entering the anion column.
8. After you are done using the repipettor tip, rinse it in milli-Q water by filling the clean “acid only” beaker with milli-Q and filling/emptying to the sink, the reservoir, several
times. Rinse the beaker out with Milli-Q and dry in the oven. Once it is dry, add parafilm and replace the beaker on its shelf.

**Column Acids**

There are different acids for anion and cation columns. There is a reason for this. Acid strength is CRITICAL for cation column performance. It is much less critical for anion columns.

For cation columns, we want to make sure that the same acid batch (dilution) is used for all samples in a batch. Both storage and wash bottles are clearly labelled with red tape indicating whether they are to be used for cation or anion chemistry. For example, in cation columns 0.65 M sulfuric acid and the 1.2 N HCl are mixed in 2 litre stock solutions and then transferred to the proper wash bottles. The stock solutions are enough for exactly three batches. If you mix and match, you will end up with odd amounts of column acids – not a good thing.

For anion columns, it is Ok to make more acid and use mixed batches if you run out mid-way through doing columns.

**Anion columns**

**NOTE:** the bottom cap on the columns must always stay on longer than the top cap or risk injecting air into the columns, destroying them and requiring replacement.

1. Check to make sure samples are dry. They may be red/yellow/brown.
2. Turn the hotplate to 60°C before doing this step so that the samples stay warm. Let the samples and hotplate cool to 60°C.
3. Take out 12 acid-washed 15 ml tubes. Label each by letter (A-L) and batch #. Place them in order in a rack.
4. Use the 6N HCl Teflon wash bottle to add about 65 ml of 6N HCl to a CLEAN ACID beaker.
5. Use the 5 ml pipette, a new tip a spill tray, and the pipette carousel.
6. Remove the first sample from the hotplate and set on a spill tray, it will be warm! Add 2.5 ml of 6 N HCl to the sample. Swirl to dissolve. Add a disposable pipettor to the beaker and use it to help break up the cake and get sample back in solution. Transfer the sample to its labelled, acid-washed 15 ml tube. DO a 2.5 ml wash of the beaker into the corresponding tube with 6N HCl.
7. Repeat in order, B-L for all the remaining samples.
8. Centrifuge ten minutes at 3500 rpm. Place the disposable pipettes in Be waste bag.
9. Place tubes in rack gently (so as not to disturb the plug of material at the bottom) and return to hood.
10. Set out the column rack with catch basins underneath each side. Remove the columns from storage and place them on the rack.
11. Remove the top caps and place them in the cap bag. Place the anion reservoirs (stored in bags) on the columns. Remove the bottom caps.
12. Let the water in the columns drain out completely.
13. **Column Stripping:** Take out the 1.2N HCl squirt bottle. Squirt in the 1.2N HCl to the 5-column volume mark on the reservoir. Fill all the columns on one side of the rack to the top (that will be about 15 ml of acid), then spin the rack and fill in the next 6 columns. This weak acid will strip any iron off the columns.
14. **Column Conditioning:** Next, add 3 bed volumes (9 ml) of 6N HCl to condition the columns. Let this volume drain through.
15. While the acid is draining, label your anion beakers with tape and the letters A-L along with the batch number.
16. After **ALL acid has drained**, place the labelled beakers under the correct column. THIS IS CRITICAL. If you don’t put the beakers under the columns now, you will lose your sample.
17. **Sample Loading:** Open up the 15 ml tube containing sample A, gently suck up the supernatant trying not to disturb the plug of material at the bottom using the pipette from the proper beaker. Try and remove as much liquid as you can from the test tube without drawing up ANY of the plug of TiO2 and other junk at the bottom. It will usually take two pulls of liquid to transfer the sample. It is OK to leave several mm of liquid above the plug. Much better to lose a bit of sample than to introduce junk into the column (which will plug the column, requiring its replacement). Get the pipette down to the frit and gently drip the supernatant into the first column. Once done, leave the pipette in the empty tube.
18. Repeat for all samples and let all samples drain into their respective beakers. The Be and Al are now moving into your anion beakers.
19. Once all samples are transferred, dispose of tubes, pipettes and caps into Be waste.
20. **Sample Elution:** When all the samples have COMPLETELY drained in, add another 3 bed volumes (9 ml) of 6N HCl to elute the remaining Be and Al into the anion beakers.

21. Add 140 ul of concentrated H₂SO₄ using a repeater to each sample. Use a 1.0 ml tip. DO THIS BEFORE placing on the rack to minimize the chance of splash and sample cross talk. It’s a CRITICAL step, if you forget the cation columns will fail.

22. Place the anion beakers in their rack on the small hotplate. The anion columns remove all Iron from the sample if done correctly.

23. Dry off at 110°C. This will take many hours, probably, overnight.

24. Return the waste bins to the column rack.

25. **Column Stripping:** Take out the 1.2N HCl squirt bottle. Squirt in the 1.2N HCl to the 5-column volume mark on the reservoir. Fill all the columns on one side of the rack (that will be about 15 ml of acid), then spin the rack and fill in the next 6 columns. This weak acid will strip any iron off the columns; you will see the draining solution is bright yellow.

26. **Column Washing:** Fill each column reservoir to top with Milli-Q and let drain completely to waste. Put the bottom cap on first. Fill the column with Milli-Q to the bottom of the textured ring. Put on the top cap.

27. Dump the waste trays into the wash hood sink VERY carefully with the water Running.

28. 1% nitric rinse the outside and inside of the trays, rinse very well with DI spray gun, dry on the counter (they will melt in the oven!) and put away.

29. Acid wash the inside of the reservoirs with 1% nitric and rinse with copious milli-Q water. Dry in the oven and replace in their bag.

30. Put the column rack in the wash hood. Rinse well with the DI spray gun to remove any acid (and Be); then acid wash with 1% Nitric spray bottle (in the hood) and rinse well with the DI spray gun. Dry on the counter.

31. Make sure the Milli-Q water with trace sulfuric is made up and ready for tomorrow morning and cation columns.

**Post-anion clean up**

1. Check that the hotplate is at 110. If not, cool it to 110. This is to prevent boiling and spatter.

2. Once the post anion drydown is complete, the samples may be dark brown if anion columns are new, may have black flecks, and will be in a thick, sulfuric acid syrup.
3. Take out the dropper bottle of 2% peroxide and the 240 ml reservoir of Milli-Q water with a trace of H2SO4. Take out the repipettor and a spill tray. Place the 25ml Milli-Q-trace sulfuric tip on the repipettor.

4. Add 7 drops of 2% peroxide to each beaker from the dropper bottle. Then, add 2 ml of Milli-Q water with a trace of H2SO4 to each beaker using the repipettor.

5. Swirl each beaker gently to dissolve the sample. The resulting solution will be yellow to reddish brown in colour. Return the sample to the hotplate and evaporate at 110 C to remove the water. Higher temperatures will result in spattering. You can use a mirror instead of moving the beaker. This will take 2 to 3 hours. As the peroxide evaporates and reacts, the samples will go from red/brown back to clear or nearly clear with little colour.

6. IF THE COLUMNS ARE NEW, repeat the peroxide/water addition a second time after which samples should look much cleaner. If they are still dark coloured, do a third repetition.

IMPORTANT NOTE: If your samples remain dark and UGLY, your peroxide is probably old. Replace with new and retreat. But, if the samples are light red/brown and clean. That is OK. It is Ti in solution with peroxide.

Cation columns

NOTE: Capping is key. The bottom cap always needs to be on longer than the top cap so that air is NEVER forced into the resin bed or else…

NOTE: Do not leave the columns dry any longer than absolutely necessary or risk having them get air bubbles and need replacement.

NOTE: Make sure you have enough of all elution solutions to do you WHOLE BATCH before you start. If not, mix new solutions. Solution concentration is absolutely KEY – do dilutions accurately or risk losing your samples.

1. Turn down the hotplate to 40°C.

2. Place cation columns in the cation column rack. Check that they are in the proper position. Check columns for air bubbles under the frit. If there are air bubbles, discard column and replace.
3. Place the waste bin under the rack. Take the top cap off, then the bottom cap to drain all the water from your columns. Add the reservoirs. Put the caps in a clean, safe place.

4. Column Conditioning: Condition the columns by filling the reservoir with 5 column volumes of \(0.65 \text{ M } \text{H}_2\text{SO}_4\) (spiked with peroxide) from the squirt bottle. Let the columns drain.

5. While the acid is draining (conditioning step), label your beryllium and titanium beakers with tape and number them A-L along with the batch number and type (Ti, Be). These are the 30 ml (tall) beakers. Label the Al beakers too; these are the 22 ml (shorter beakers). Label the Ti beakers in red; the Al with orange and the Be in blue.

6. Take out the box of disposable pipettes.

7. One at a time, starting with sample “A”, bring up the samples in 2 ml Milli-Q water with trace \(\text{H}_2\text{SO}_4\) and add 7 drops of 2\% \(\text{H}_2\text{O}_2\) to each sample. Use the repipettor to deliver the Milli-Q water with trace \(\text{H}_2\text{SO}_4\). The sample will be yellow/orange/red in colour. Use a dedicated disposable pipettor to make sure the sample is well mixed.

8. CRITICAL – examine the sample in the pipette. Do you see any small, needle like crystals? If so, STOP. Put the sample back in its beaker, get a clean acid washed 15 ml tube, and centrifuge the sample to remove the crystals. They are likely gypsum. After centrifuging, transfer the supernatant only to the column as below. Discard the tube (and the crystals) as Be waste.

9. **Loading Sample:** Add the sample gently to the frit of its respective column using the pipette. CRITICAL – double check that you are loading the right sample into the right column, go letter by letter.

10. **Rinsing Sample beakers:** Add another 2 ml of Milli-Q water with a trace of \(\text{H}_2\text{SO}_4\) to the sample beaker and then add this solution to the proper column. Use a 5 ml variable to deliver the 2 ml Milli-Q water with trace \(\text{H}_2\text{SO}_4\) shot. DOUBLE CHECK that you are adding the right sample to the right column. Once the sample is added, put the empty beaker in a wash jug and dispose of the pipette as Be waste.

11. **Repeat for the remaining samples in order from B-L**

12. Let the solutions drain into the columns until the headspace is clear.
13. Remove the waste container and put the labelled Ti beaker (tall, 30 ml) under each column. Double check to make sure they are correctly located.

14. Titanium Elution: Use the squirt bottle to SLOWLY add $0.65 \text{ M } \text{H}_2\text{SO}_4$ to the reservoir, add 5.5 bed volumes. Let the columns drain until the liquid is at the top of the frit. **Watch this elution!** The red band of Ti should move through the column and completely elute. If there is any yellow colour remaining in the lower tip of the column (this happens with high Ti samples) decant several ml from the Ti beaker to waste and add another 5 ml of $0.65 \text{ M } \text{H}_2\text{SO}_4$ to that column only! This will complete removal of Ti with minimal loss of Be. Once all columns have drained, remove, cap and store Ti beakers under the hood until yield checks are complete. Remember that you will need to empty and wash these beakers after verifying sample yield and purity.

15. Place the Be beakers (tall, 30 ml) under the column rack in their proper numbered positions. Double check to make sure they are correctly located.

16. Beryllium Elution: Use the squirt bottle to SLOWLY add $1.2 \text{ N } \text{HCl}$ to each reservoir. Add 5.5 bed volumes of acid. When the samples have completely drained through the columns, transfer the beakers to the dry block placing them in the deeper wells in A-L order.

17. Nitric Addition: Add 7 drops of 8M Nitric Acid to each Be sample beaker. This step is rumoured to reduce boron in the samples.

18. Place the Al beakers (shorter, 22 ml) under the column rack in their proper numbered positions. Double check to make sure they are correctly located.

19. Aluminium Elution: Use the wash bottle to SLOWLY add 4 bed volumes (20 ml) of $4\text{N HCl}$. When the samples have completely drained through the columns, set all the beakers on the small hotplate in the shallow holes to dry down.

20. Dry down overnight with the hotplate set at 110°C.

21. Column Stripping: Replace the waste bin. Add 4 additional column volumes of $4\text{N HCl}$ and let it drain fully. This strong acid will strip any Be and Al off the columns.

22. Column Washing: To rinse the columns and remove any and all acid, fill the reservoir completely with milli-Q water and let it drain.

23. **To store the column:** Remove the reservoirs. Cap the bottom first, fill column with water to bottom of textured area, then install the top cap.
24. Dump the waste trays into the wash hood sink with the tap running for dilution.
25. 1% nitric rinse the outside and inside of the trays, rinse very well with DI spray gun, dry on the counter (they will melt in the oven!) and put away.
26. Acid wash the inside of the reservoirs with 1% nitric and rinse with copious milli-Q water. Dry in the oven and replace in their bag.
27. Put the column rack in the wash hood. Rinse well with the DI spray gun to remove any acid (and Be); then acid wash with 1% Nitric spray bottle (in the hood) and rinse well with the DI spray gun. Dry on the counter.

**Redissolving**

1. After drydown, there should be a small bead of clear liquid in the base of the Be beakers (this is H₂SO₄). Al should form a small, dry, white cake.
2. Turn hotplate down to 60 and let samples cool to 60°C.
3. Take out the repipettor and the 1% Nitric tip. Extract 50 ml (filling the reservoir) from the 1% Nitric acid beaker labelled “for precip only”.
4. Add 8 ml of 1% Nitric acid to each sample beaker. Then cap TIGHTLY and return to hotplate letting sit for at least 30 minutes to redissolve.
5. Take out 24 acid washed, blue cap tubes. Label 12 tubes for Al, and 12 tubes for Be along with the sample letters, sample name, and batch number. These are for final precipitation. Rack the tubes in order (A-L) and by element (Al and Be). LABEL the caps by LETTER. For the Al samples use orange tape. For the Be samples use blue tape.
6. Repeat for all Be and then for all Al fractions. MAKE SURE ALL LIDS are labelled by letter.
7. Take out 24 unwashed, purple tubes and caps and set in a purple rack. Take out a second empty purple rack. These will be used for yield tests to ensure that the samples are clean and that the Be and Al are where they belong.
8. After the samples have redissolved for 30 minutes, vortex each sample beaker for at least five seconds upright and another 5 second inverted. This is to ensure that the sulfuric acid goes back into solution.
9. Take the first Be beaker. Drain solution to a new, acid-washed, blue capped tube. THIS IS YOUR SAMPLE. Cap the tube tightly.
10. Transfer the label from the beaker to the PURPLE tube. This tube remains EMPTY and will be used for the yield test. Drop the beaker and its lid into the wash bin. Fill with 1% Nitric Acid and sonicate overnight.

**Removing yield testing aliquots**

**NOTE:** It is critical to avoid cross-talk. Make sure your pipette body does not touch the edge of the test tube. If it does, wipe down the pipette body with Milli-Q and a wipe to avoid sample cross talk.

1. Place the pipette carousel in the hood.
2. Take out the 10-100 ul micropipettor and box of tips. Hang the pipette on the carousel. Set tips on cart.
3. Take out the 50-1000 ul variable pipettor and box of tips. Hang the pipette on the carousel. Set tips on cart.
4. Take out 5 ml variable pipettor and a new tip and the weak H₂SO₄ “Yield Test” solution from the white acid cabinet. Put 130 ml of “Yield Test” solution into a clean acid beaker. Hang the pipette on the carousel.
5. Arrange racks and tubes in a way that makes sense to you and prevents any sample confusion.
6. Place a new tip on the 1ml and 100 ul pipettes.
7. Uncap tube A containing the first Be sample. Use the 1ml pipette to remove 200 ul from the Be fraction. Add it to the Be yield tube for sample A. Cap the sample tube and set aside in another tube rack for later precipitating. **DISCARD THE 1 ml TIP IMMEDIATELY to Be waste and hang the pipette on the carousel.**
8. Add 5 ml of weak H₂SO₄ solution to the ICP yield split. Cap the tube and set aside in the second purple rack.
9. Use the micropipettor and remove 50 ul from the Al fraction of sample A and add it to the labelled purple capped tube. Cap the sample tube and set it aside. Discard the pipette tip.
10. Add 5 ml of weak H₂SO₄ solution to the ICP yield split for Al. Cap the tube and set aside in a rack.
11. Return to step 6 and repeat for all samples.
REMEMBER TO CHANGE TIPS on the micro and 1 ml pipettes between EVERY sample. This is ABSOLUTELY key to prevent cross talk. Reuse the 5 ml tip.

12. Shake and VORTEX each yield sample to ensure mixing. This is a CRITICAL step to get good data otherwise the ICP autosampler will not sample a uniform solution and results could be biased high or low.

13. Place the yield tubes in a 25 hole foam or purple plastic rack. Use a piece of tape to label over the top of the tubes in their rack with the words YIELDS, BATCH-XXX.

14. Put the rack and tubes in the white acid storage cabinet.

Precipitating and Drying Hydroxide Gels

1. Add one drop of methyl red to each tube. This is a pH indicator (changes at about pH=6) that allows us to know easily when the solution is basic and the hydroxides of Be and Al have formed.

2. Start with Be. Use the 30% NH₄OH dropper bottle and add 10 drops to the first tube of Be. Cap, shake and look for the colour to change to yellow. If there is no colour change, add one more drop, shake again. Keep adding drops one at a time until the colour just changes from red to yellow. Now, shake to ensure the sample is well-mixed and stays yellow. Then add one more drop of 30%. Shake sample very well – check colour again.

NOTE: BeOH takes more base to neutralize because of the Sulfuric Acid left over after elution.

3. For Al, do the same as in #2 above but add ONLY 3 drops of 30% to the first tube of Al then titrate dropwise.

4. Set samples overnight if possible and recheck colour the next day. If they are no longer yellow, add more NH₄OH.

5. Centrifuge for 10 minutes at 3500 rpm.

6. STOP – if you do not see a pellet/gel in the bottom of the tube, check the pH with pH paper (do this by placing the pH paper on a watch glass and using a disposable transfer pipette to deliver liquid to the paper).

DO NOT put the paper in the tube. Make sure solution pH is 8 adjusting with nitric acid and NH₄OH. SHAKE, RE-CENTRIFUGE. You should now see a pellet of gel unless the sample has been lost.
7. Make a note on the batch sheet.
8. Decant liquid to sink or waste beaker
9. Add 10 ml of Milli-Q water, VORTEX, check and see that the entire pellet is dispersed (no chunks). This washing removes soluble cations such as Na and Ca. **THIS IS A CRITICAL STEP.** If you forget to vortex the wash, the gels will not dry down to a pellet.
10. Centrifuge for 10 minutes at 3500 rpm and decant leaving the gel at the bottom.
11. To dry Be samples, first check to see if there is water over the gel that did not come out with decanting. If there is water, use a new disposable pipette for each sample to remove the water (if the water is not removed, the sample will not make a solid pellet but rather will coat the bottom of the tube).
12. Once the water is gone, take off the cap of tube A and place it in the dry block in standard A-L order. Repeat for all other tubes and arrange caps in a spill try upside down in order. **DO NOT PLACE TUBES with GELS IN THE OVEN to dry.**
13. Save the Al fractions as washed gels. Do not dry down until ready to pack. Store these Al gels in the large plastic box under the counter in white foam holders with labels on the side and top indicating the batch number. Update the Al gel inventory.
14. Set the hotplate to 65°C and NO HIGHER. If you use a higher temperature, the gels will not form small pellets. This will take overnight at least. The next day, ramp the hotplate to 98 and leave the tubes for at least several hours, all day or overnight is better. Use the mirror to **ensure all drops are gone from the tube walls before capping.**
15. Once samples are dry, cap with the proper cap (check letters) and set next to the glove box. Make sure the tubes are racked in order and add a piece of tape on the top indicating the batch number and the word, “Dried”
16. Dry down when the hood is unused to prevent sample cross talk. Don’t dry down when fuming acid.

**FINAL STUFF**
1. After running and verifying yields on the ICP, dump and clean the Ti beakers ASAP.
2. Try and run Aliquots promptly and reduce the data.
3. Only after all data are entered, colour the file name for the batch sheet blue or yellow to match the hood in which the samples were run.
4. Finish cleaning, drying and putting away all labware.

**Principles of making acid and standards**
- Concentrations matter: do the same thing every time.
- Add acid to water. Operationally this often means measuring in some water to the container, adding the requisite acid, and measuring in the remaining water.
- Agitate very well after making up the acid and before using
- Always work in the hood and with a spill tray under your vessels.

1. **Ga/Y Spike recipe (DO NOT MAKE THIS UP ALONE, ASK PAUL FOR HELP)**

   This is made up in a 4 litre Nalgene wide mouth jar and lasts for many batches (about 30 batches). The concentration of Ga and Y are absolutely crucial and need to be matched to the standards or the internal standard correction will be bogus.
   a. Dump any residual solution from the stock bottle and DO NOT RINSE the bottle.
   b. Add several hundred ml of Milli-Q water to the volumetric flask.
   c. Use 5ml variable pipette to add 20 ml Aristar Plus concentrated Sulfuric acid to the water in the volumetric flask.
   d. Mass 40.47 grams of Y standard into a clean, dry 125 ml HDPE bottle. This is 40 ml of standard in 2% nitric at density 1.0117 gms/cc. Pour bottle into the volumetric flask and rinse three times with Milli-Q water into the flask.
   e. Mass 40.47 grams of Ga standard into a clean, dry 125 ml HDPE bottle. This is 40 ml of standard in 2% nitric at density 1.0117 gms/cc. Pour bottle into the volumetric flask and rinse three times with Milli-Q water into the flask.
   f. Top up the volumetric to the 2000 ml line and add to the stock bottle.
   g. Fill the 2000 ml volumetric flask with 2 litres of Milli-Q and add to the stock bottle. This functions as a rinse.
   h. Agitate the stock bottle very well for a minute.
   i. Weak acid wash the volumetric flask twice and rinse carefully with copious Milli-Q water. Let air dry on counter then cap and put away.

2. **Acid recipes**
a. Anion acid – **1.2 N HCl**, to make 500 ml in teflon wash bottle, add 50 ml of concentrated Aristar Plus HCl and fill (not precise acid dilution). Remake when needed.

b. Anion acid – **6 N HCl**, to make 500 ml in teflon wash bottle, add 250 ml of concentrated Aristar Plus HCl and fill (not precise acid dilution). Remake when needed.

c. Post anion acid – **trace sulfuric**, make in 250 ml teflon jar, fill jar with milli-Q water and add 60 ul (yes, that’s micro litres) of Aristar Plus concentrated sulfuric acid. Remake every two batches.

d. Post anion oxidize, **2% Peroxide**, make in 30 ml dropper bottle, 2 ml of 30% peroxide and fill with Milli-Q. Peroxide degrades over time. Replace every few months.

e. Cation acid - **1.2 N HCl**, to make 2000 ml in plastic HDPE wide mouth bottle, add 210 ml of concentrated Aristar Plus HCl and 1790 ml of Milli-Q water (measure acid and water in 500 ml graduated cylinder). Remake every 3 batches. As needed, use this stock to refill Teflon wash bottles.

f. Cation acid – **0.65 M Sulfuric acid** with peroxide, to make 2000 ml in plastic HDPE wide mouth bottle, add 70 ml of concentrated Aristar Plus Sulfuric and 1920 ml of milli-Q water and 10 ml of 30% peroxide (measure acid and peroxide in 50 ml graduated cylinder and water in 500 ml graduated cylinder). Remake every 3 batches. As needed, use this stock to refill Teflon wash bottles.

g. Cation acid – **4 N HCl**, to make 500 ml in teflon wash bottle, add 170 ml of concentrated Aristar Plus HCl and fill to ring (not precise acid dilution, this dilution can be eyeballed). Remake every batch.

h. Post cation, dry off acid, **8N Nitric**, to fill 30 ml dropper bottle add 15ml Milli-Q water and then 15 ml concentrated Omnitrace Nitric Acid (not precise acid dilution). Lasts for many, many batches.

i. Precipitation acid – **1% Nitric Acid**, to make in 250 ml teflon jar, fill jar with Milli-Q water and add 3 ml of concentrated Omnitrace Nitric Acid. Remake every batch.

j. Precipitation base – **15% NH₄OH** to make 30 ml dropper bottle, add 15 ml of 30% NH₄OH and fill to top.

k. Precipitation base – **30% NH₄OH**, fill directly from stock solution bottle (not precise acid dilution, this dilution can be eyeballed).
3. **Yield solution**
   a. Add 40 ml concentrated Aristar Plus Sulfuric and fill with milli-Q water in 4 litre stock solution jug.

4. **Standards**
   b. **Quartz purity standards.** We make volumetrically a stock solution of 100 ppm cations using 25 ml each of Al, Be, K, Na, Ca, Mg, Fe and Ti SPEX 1000 ppm standards. These eight standards are added to a 250 ml HDPE bottle and 50 ml DI is added. We make the four working standards using the 1% Sulfuric acid solution used for yield tests and varying amounts of the stock solution.
      - 1 ppm, 5 ml stock in 500 ml
      - 2 ppm, 10 ml stock in 500 ml
      - 4 ppm, 20 ml stock in 500 ml
      - 8 ppm, 40 ml stock in 500 ml
   c. **Aliquot standards.** These four standards are made and stored in 2000 ml glass volumetric flasks. The idea is to make a lot of standard, so it can be used for many batches. Storage in glass prevents evaporation. The internal standard will correct for small amounts of evaporation.
      - First, we made up 4 litres of solution to add to aliquots. This contains some sulfuric acid but not the entire amount to matrix match with standards because the aliquots are dried down with some sulfuric acid already and our goal is that the final aliquot dilutions have the same concentration of sulfuric acid as the standards. This aliquot solution is 4 litres (in a widemouth HDPE bottle) of 0.5% Sulfuric Acid. This requires 20 ml of sulfuric acid added with graduated cylinder and 20 ml each of Y and Ga. The Y and Ga are added gravimetrically by pipetting (using 5 ml variable) into the graduated cylinder on the balance. With a density of 1.0117, we add 40.47 g of standards. This solution is remade as needed, about every 30 batches.
      - Second, we made up the four standards. We did this by adding some milli-Q water to each of the four pre-labelled volumetric flasks. Then, we massed the proper amounts of Al and Be standard into a clean, dry 250 ml HDPE bottle as well as proper amounts of Ga and Y standards to match the aliquot dilution solution. Note
that Al carrier is in 2% HCl and Be carrier is in 2% Nitric Acid. We poured the standards into the volumetric flask. Then repeatedly rinsed the HDPE bottle with 1% Sulfuric Acid into the volumetric flask. We then topped up the volumetric flask with 1% Sulfuric Acid.

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<th>Ga (mass std)</th>
<th>Y (mass std)</th>
<th>Be (mass std)</th>
<th>Al (mass std)</th>
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<td>20.234</td>
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d. Carrier calibration standards.
These are spiked with Ga and Y for ICP internal standardization. We make a blank, 2 and 4 ppm. These are made mass/mass 100 ml at a time. First, we made a stock solution, 500 total ml of 10 ppm Ga and 10 ppm Y in 2% nitric acid. This was done by massing in 5.07 grams of standard (density 1.0117 g/cc). The we made a second solution, just 2% nitric acid (14.3 ml in 500 ml Milli-Q water). The we made 2 and 4 ppm standards by adding 200 ul of Be (1000 ppm, about 0.200 g) and adding 400 ul of Be (about 0.400 g) then adding an ml each of Y and Ga (which were massed. The total mass of the solution was brought to 101.17 (100 ml). See cosmolab start up notebook for original details.

e. Column Loading
We reuse and regenerate columns. Columns are replaced only if they develop air bubbles or have been compromised in some other fashion. Because of the fritting arrangement, columns themselves are not emptied but disposed of as trash when their time has come.

f. Loading Anion Columns (done only when columns need replacement)
1. Get out the anion resin (Arcos Dowex 1-8 200-400 mesh). Get out a spill tray, a clean acid beaker, and a disposable pipette.
2. Shake resin to slurry.
3. IF columns are new or dry, place half an ml of ethanol onto each column to wet the frit (if you forget the ethanol, the columns won’t drip). Make sure to IMMEDIATELY clean up any ethanol drips. It will destroy the plastic racks by cracking. Let all the ethanol drip through.

4. Load the columns – always load into standing water to reduce the chance of bubbles. Load the first shot of resin into the six columns along the front of the rack. Let the resin settle from suspension. Then, add enough resin to fill the column to the base of the first shoulder. If you add too much resin, pipette it out. Repeat on the back side.

5. After the columns have all been loaded with the same and correct amount of resin, but before the water has drained out, add the upper frit pushing it down through the water until it is uniformly 1-2 mm above the resin bed.

g. Loading Cation columns (done only when columns need replacement)

1. Set out the column carousel and get out the reference column.

2. Set out the 12 columns that you will use; take out 12 frits and the frit pusher. Mark the 5 ml level on each column using a sharpie. Put a bottom cap on the column.

3. One at a time, fill the column 80% with Milli-Q water. Tap the column to dislodge any air bubbles. Then float the frit on the water and use the frit pusher to slowly push the frit down the column until it is flat and square on the base. Repeat for all columns loading them after the frits are in onto the carousel.

4. Get out the CATION resin (Arcos Dowex 50WX8 200-400 mesh). Get out a spill tray, a clean acid beaker and a disposable pipette.

5. Shake resin to slurry.

6. Load the columns with resin – always load into standing water to reduce the chance of bubbles. Add about 2ml of Milli-Q water into the column. Then, load the first shot of resin into the columns. Let the resin settle from suspension. Then, add enough resin to fill the column to the 5 ml mark. If you add too much resin, pipette it out. Once all columns are at 5 ml, then add more Milli-Q water, resuspend the resin and let it settle out smoothly.

7. After the resin has settled but before the water has drained out, add the upper frit pushing it down through the water until it is uniformly 1-2 mm above the resin bed.
## E: AMS RESULTS

<table>
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<tr>
<th></th>
<th>ratio raw</th>
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<th>stat</th>
<th>sample blk corr</th>
<th>uncm (1s)</th>
<th>sample blk corr normalized</th>
<th>carrier (mg 9-Be)</th>
<th>N_10_TO T+BLK</th>
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|          |          |      |      |      |          |                            |                   |               |

**Notes:**

- **Ratio raw:** The ratio of the sample to the standard.
- **Sdom:** Statistical uncertainty due to blank.
- **Stat:** Statistical uncertainty due to measurement.
- **Sample BLK CORR:** Correlation correction applied to the sample.
- **Unc (1s):** Uncertainty at the 1-sigma level.
- **Sample BLK CORR Normalized:** The normalized correlation of the sample.
- **Carrier (mg 9-Be):** Carrier amount of 9-Be.
- **N_10_TO T+BLK:** N value at 10 times the total blank.

**Units:**

- **Ratio:** Dimensionless.
- **Sdom, Stat:** Statistical uncertainties in percentage.
- **Sample BLK CORR:** Correction applied to the sample.
- **Unc (1s):** Uncertainty at the 1-sigma level, in percentage.
- **Sample BLK CORR Normalized:** Normalized correlation of the sample.
- **Carrier (mg 9-Be):** Carrier amount of 9-Be, in mg.
- **N_10_TO T+BLK:** N value at 10 times the total blank, in mg.
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## Online erosion rate calculator v3 results

### Version info:
- wrapper: 3.0
- erates: 3.0
- muons: 3.0-dev
- validate: validate_v2_input.m - 3.0
- consts: 3.0.4

### Erosion rate results:

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<th>Internal uncert (m/Myr)</th>
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In contrast to exposure-age results, here multiple-nuclide diagrams use only St scaling for normalization.

Exposure Ages
## Online exposure age calculator v3 results

### Version info:
- wrapper: 3.0.2
- get_age: 3.0.2
- muons: 1A, alpha = 1
- validate: validate_v3_input.m - 3.0
-consts: 3.0.4

### Calibration data:
- Calibration data set: Default calibration data set

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