URANIUM-LEAD GEOCHRONOLOGY OF GRANOPHYRES FROM THE ARCHEAN STILLWATER COMPLEX, MONTANA (USA): CHARACTERIZATION OF URANIUM-BEARING ACCESSORY MINERALS (ZIRCON, TITANITE, RUTILE) AND PRELIMINARY DATING RESULTS

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Abstract

The ca. 2.7 Ga Stillwater Complex is a mafic-ultramafic layered intrusion located in the Beartooth Mountains of southwest Montana. The intrusion is dominated by mafic-ultramafic cumulate rocks, but also contains volumetrically minor granophyres that were emplaced as late-stage differentiates within the plagioclase-rich Banded Series of the complex. The granophyres consist primarily of albite (or oligoclase) + quartz and display a wide variety of textures, including granophyric, graphic, equigranular, and pegmatitic. The granophyres are discordant bodies and typically range in thickness from a few centimetres up to tens of metres. High-U accessory minerals (zircon, titanite, rutile) are present in the granophyres and were separated from whole rock samples for characterization by scanning electron microscopy (SEM) and age determination by U-Pb geochronology using isotope dilution thermal ionization mass spectrometry (ID-TIMS). The chemical abrasion pre-treatment technique (annealing and leaching) was employed for determining the age of single grains of zircon.

In this study, four separate granophyres were sampled from different stratigraphic levels in the Banded Series (lower, middle, and upper). Three samples yielded mostly euhedral prisms of zircon (ranging from 100-300 μ m) that are highly metamict due to very high U-contents (87.3 to 1438.2 ppm). The U-Pb systematics of these zircon grains have been strongly disturbed since crystallization due to self-irradiation (metamictization) and subsequent fluid infiltration events, which resulted in substantial Pb-loss. In contrast, zircon grains from a pegmatic core to a gabbroic pegmatoid that cross-cuts the layered cumulates of the Lower Banded Series are clear, interstitial, pale-pink, high-quality grains, of low to moderate U-content (76.2 to 237.1 ppm). A U-Pb concordia age of 2709.6 \pm 0.8 Ma (2 σ) was determined from this sample and is interpreted as a minimum age for the crystallization of the Stillwater Complex. This age is consistent with previously published U-Pb zircon geochronology of basal sill and dikes that yielded ages mostly in the range from 2710 to 2712 Ma and suggests that the Stillwater Complex was emplaced within a few million years.

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1.0 Introduction

The Archean Stillwater Complex in the Wyoming Province of Montana (Figure 1) is one of the world's largest layered intrusions and is host to a rich platinum group element (PGE) deposit known as the J-M Reef. Determining the precise age of crystallization of the Stillwater Complex has been difficult due to the relative lack of U-bearing accessory minerals in these maficultramafic cumulate rocks. The currently accepted age of the Stillwater Complex is 2705 ± 4 Ma by Premo et al. (1990). However, this date is based on combining the results of select multigrain fractions of zircon-baddeleyite from two different samples, which is no longer an accepted method for rigorously assessing the precise age of an igneous rock. In addition, U-Pb geochronology of basal sills and dikes associated with the Stillwater Complex are ca. 2010 Ma, which suggests that these may be several distinctive ages of magmatism in the complex, assuming that the 2705 Ma age is correct (Premo et al, 1990).

Granophyric dykes occur within the Stillwater Complex and intrude layered cumulate rocks in the Banded Series of the complex (Czamanske et al., 1991). In this study, we report preliminary U-Pb zircon (ZrSiO₄) dates by the single-crystal chemical abrasion (CA) ID-TIMS technique for four different granophyric dykes. In conjunction with scanning electron microscope (SEM) imaging and U-Pb cooling ages from coexisting titanite (CaTiSiO₅) and rutile (TiO₂), these geochronological results are used to evaluate the duration of emplacement and crystallization of the Stillwater Complex, which may have implications for events such as the formation of the J-M Reef.

2.0 Regional Geology

The ca. 2.7 Ga Stillwater Complex (Figure 1), one of the largest mafic layered intrusions in the world, is exposed over approximately 180 km² at the northern edge of the Beartooth Range in southern Montana, which is one of the major exposed blocks of the Archean Wyoming Province. The intrusion is approximately 36 km in length, has a width of approximately 8.5 km, and a minimum downslope extension distance of 8 km. The Stillwater Complex was emplaced at a depth of 10-15 km (McCallum, 1996) into a folded sequence of Archean sedimentary rocks that was subsequently metamorphosed to a hornfels assemblage at the time of magmatism (Blakely et al., 1984). The Stillwater Complex is locally exposed between the Boulder River and Chrome Mountain and in the Mountain View area (Figure 1) due to strong Laramide deformation that exposed the complex and resulted in about 5.2 km of uplift and subsequent erosion (McCallum, 1996).



Figure 1. Schematic geologic map of the Archean Stillwater Complex from McCallum (1996). Inset diagram shows the regional setting of the Stillwater Complex with relation to major Archean blocks.

Regional gravity and magnetic surveys in this area indicate that the complex extends at a depth approximately 25 km to the northeast of the Beartooth Mountains front (Figure 1, inset) (Blakely et al, 1984). From the West Fork to the main Stillwater River (Figure 1), a younger quartz monzonite intrudes the complex east of the Stillwater River along the Bluebird Thrust (McCallum, 1996). To the east of the Stillwater River, the complex is intruded by the same quartz monzonite. Along the northern margin of the complex, Paleozoic and Mesozoic sedimentary rocks overlie the complex along a mainly unconformable contact (McCallum, 1996). Between the West Fork and the Stillwater River, this unconformity is marked by the Horseman Thrust (Figure 1).

3.0 Geology of the Stillwater Complex

The Stillwater Complex is subdivided into: the Basal Series, Ultramafic Series, and Banded Series (which is further divided into the Lower Banded Series, Middle Banded Series, and Upper Banded Series) (McCallum, 1996), based primarily on the distribution and composition of cumulus minerals. These main units have been further subdivided into zones (Figure 2) and subzones. Below, the general characteristics of these series are briefly outlined to provide an overview of how the Stillwater Complex was assembled.

3.1 Mineralogy

The most abundant primary cumulus minerals in the Stillwater Complex are olivine, orthopyroxene, clinopyroxene, inverted pigeonite, plagioclase, and chrome spinel (McCallum, 1996). Table 1 indicates a full classification of all rock names used in the Stillwater complex and their associated cumulus and postcumulus minerals.

(Haupted Hom Mecana	iii 1770).	
Rock Name	Cumulus Minerals	Postcumulus Minerals
Peridotite	Ol (+/-Chr)	Opx, Cpx, Plag, Phl, (Amph, Ap)
Harzburgite	Ol, Opx, (+/-Chr)	Cpx, Plag, (Phl, Amph, Ap)
Chromitite	Chr (+/-Ol)	Opx, Cpx, Plag, (Phl, Amph, Ap)
Bronzitite	Opx	Plag, Cpx,, (Qtz, Phl, Ap)
Norite	Plag, Opx/Pig	Cpx, (Ap, Qtz)
Olivine Gabbro	Plag, Cpx, Ol	Opx (Ap)
Gabbronorite	Plag, Opx/Pig, Cpx	(Qtz, Ap, Mt)
Troctolite	Plag, Ol	Opx, Cpx (Ap)
Olivine Gabbronorite	Plag, Opx, Cpx, Ol	(Ap)
Anorthosite	Plag	Opx/Pig, Cpx, Qtz, (Mt)

Table 1, Description of rock types and their associated cumulus and postcumulus minerals. (Adapted from McCallum 1996).

Abbreviations: Ol = Olivine; Chr = Chromite; Opx = Orthopyroxene; Pig = Pigeonite; Cpx = Clinopyroxene; Plag = Plagioclase; Qtz = Quartz; Ap = Apatite; Phl = Phlogopite; Mt = Magnetite; Amph = Amphibole. Minerals in parentheses indicate minor phase minerals that may not always be present.



Figure 2. Composite stratigraphic section of the Stillwater Complex depicting approximate thickness of the series and their associated zones (modified from McCallum, 1996). Modal stratigraphy based on percentage of cumulus minerals, and types of cumulus minerals present in different lithologies.

3.2 Basal Series

The Basal Series, which is denoted by the area below the layered series, is the only series in the Stillwater Complex where olivine does not appear as a volumetrically significant cumulus mineral (Page, 1979). It is laterally continuous with a local vertical thickness of 100 m. The Basal Series has not been subdivided into smaller zones, but does include a sill and dike suite that cross-cuts the base of this series. The main lithology is a bronzitite cumulus with hornfels xenoliths of surrounding host rock. The bronzitite exists mainly in the top of the Basal Series and is underlain by a variety of rock types that are mostly norites, but also include anorthosite, gabbro, and peridotite (McCallum, 1996). The rocks of the Basal Series intrude the underlying metamorphic hornfels rocks (Page and Zientek, 1985). The contact is fairly irregular, which suggests emplacement of the Stillwater magma along an unconformity (McCallum, 1996). Based on isotopic studies (Premo et al., 1990), the sill and dike suite has been interpreted as the parent magma for the Stillwater Complex.

3.3 Ultramafic Series

The base of the Ultramafic Series is placed at the first appearance of cumulus olivine and the top of the series in placed where plagioclase first appears as a cumulus mineral (Figure 2). In most areas, the Ultramafic Series overlies the Basal Series; however there are sections where it is in direct contact with basement rock (Blakely et al, 1985). The Ultramafic Series is divided into two zones: a lower Peridotite Zone, which contains abundant cumulus olivine, orthopyroxene, and chromite, and an upper Bronzitite Zone, which consists primarily of cumulus orthopyroxene (Jackson, 1961). The Peridotite Zone consists of repetitive cyclical units of peridotite-harzburgite-bronzitite; approximately 21 cycles occur within the Peridotite Zone. This cryptic variation is interpreted to result from steady influxes of magma form the parent source into the chamber (McCallum, 1996). The Bronzitite Zone, however, is a much more uniform section with the exception of a few thin layers containing cumulus olivine and chromite.

3.4 Lower Banded Series

The Lower Banded Series is composed mainly of norites and gabbronorites and is host to the platiniferous J-M Reef, which is the contributor of platinum group elements for mining purposes in the Stillwater Complex. The lower contact of the Lower Banded Series is marked by the first appearance of cumulus plagioclase, whereas the top of the unit is based on the first appearance of a thick anorthosite section (Figure 2). This series has been divided into six zones: Norite-I (N-I), Gabbronorite-I (GN-I), Olivine-bearing-I (OB-I), Norite-II (N-II), Gabbronorite-II (GN-II), and Olivine-bearing-II (OB-II) (McCallum, 1996). The cumulus plagioclase within the Lower Banded Series becomes less An-rich (i.e. more sodic) closer to the top of the Lower Banded Series and parallels a decrease in the mol % Mg/Mg+Fe in pyroxene (McCallum, 1996), which is indicative of fractional crystallization and accumulation.

3.5 Middle Banded Series

The Middle Banded Series is relatively rich in plagioclase compared to the lower and upper members. Cumulus plagioclase comprises 82% by volume of the Middle Banded Series with olivine and augite being the most common cumulus mafic minerals (McCallum, 1996). The main rock types are anorthosite, troctolite, and olivine gabbro. Throughout the section, the olivine abundance is very low at less than 10 modal % (Meurer et al., 1996). Plagioclase is 2-3 times larger in grain size than plagioclase found in the Lower or Upper Banded Series and shows very complex zoning (McCallum, 1996). Plagioclase compositions are very uniform (An = 74.5-80) throughout the section (Meurer et al., 1996). McCallum et al. (1980) suggest that this resulted from buffering of the plagioclase composition due to a very high abundance of plagioclase relative to intercumulus liquid.

3.6 Upper Banded Series

The Upper Banded Series is very similar to the Lower Banded Series and comprises mainly norites and gabbronorites. The Upper Banded Series has been divided into two zones: Olivine-bearing Zone V (OB-V), and the Gabbronorite-III Zone (GN-III) (McCallum, 1996).

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Similar to the Lower Banded Series, plagioclase in the Upper Banded Series decreases in mol% An upsection, which is indicative of fractional crystallization and accumulation. This difference between the Lower/Upper Banded Series and the Middle Banded Series may be explained as the lack of magma input into the Middle Banded Series, which allowed for convection and mechanical mixing and the development of uniform plagioclase composition, whereas the Lower and Upper Banded Series are characteristic of influxes of magma and venting of fractionated magma from the chamber (McCallum, 1996).

3.7 Granophyres

The granophyres of the Stillwater Complex are restricted to the Banded Series, and are volumetrically insignificant compared to the complex itself (Czamanske et al., 1991). The granophyres are cross-cutting intrusions that typically range in thickness from a few centimetres up to several tens of metres. These rocks are characterized by high whole rock SiO₂ contents (~78 wt%) and low amounts of K-feldspar (whole rock K₂O ~ 0.12 wt%) with the main feldspar being albite or oligoclase (Czamanske et al., 1991). In the larger granophyre bodies that have been termed "alaskite", the K₂O contents are higher ranging from 1.9-5.0 wt% (Czamanske et al., 1991). Textures within these granophyres range from equigranular to granophyric and graphic intergrowths of plagioclase and quartz and have been interpreted as late-stage melts in equilibrium with high-pressure chloride solutions (Czamanske et al., 1991). These rocks have been shown to contain anomalous amounts of Ca, possibly from the albite component present in the plagioclase from the surrounding Banded Series, as well as high amounts of incompatible elements would suggest that these melts are late-stage high fractionated melts. The general term "granophyre" will be used to describe all samples examined in this study.

4.0 Previous Geochronology

4.1 Geochronology of the Stillwater Complex

Due to the excellent exposures, presence of igneous layering, and significant mineralization (Cr from chromitites and PGE from the J.M. Reef), the Stillwater Complex has been heavily studied for both geochronology and for understanding its crystallization history. Despite numerous studies, the age of the Stillwater Complex is still relatively poorly constrained. A list of different methods and resulting dates produced can be seen below in Table 2.

Isotope System	Sampling method	Age (Ma)	References
K-Ar	Plagioclase	2000-3200	[Kistler et al., 1969]
K-Ar	Phlogopite	2540-2640	[Kistler et al., 1969]
Rb-Sr	Whole Rock	2108-2608	[Fenton and Faure, 1969]
Rb-Sr	Whole Rock*	2522-2822	[<i>Powell et al.</i> , 1969]
Rb-Sr	Whole Rock*	2647-2737	[Mueller and Wooden,1973]
Sm-Nd	Whole Rock, Plagioclase, Bronzite,	2693-2709	[DePaolo and Wasserburg,1979]
	Augite		
Sm-Nd	Whole Rock	2862-2930	[Tatsumoto and Coffrant,1980]
Sm-Nd	Whole Rock	2708-2776	[Tatsumoto and Coffrant,1980]
Sm-Nd	Whole Rock	2782-2814	[Tatsumoto and Coffrant,1980]
U-Pb	Zircon	2700-2750	[Nunes and Tilton, 1971]
Pb-Pb	Whole Rock	2650-2674	[Manhes et al., 1980]
U-Pb	Zircon	2596-2770	[<i>Lambert et al.</i> , 1985]
U-Pb	Zircon, Baddeleyite	2701-2709	[Premo et al., 1990]
Re-Os	Chromitite	2660-2820	[Marcantonio et al., 1993]

Table 2: A summary of age determinations of the Stillwater complex using different methods and samples. Adapted from Selkin et al. (2008).

(* denotes samples taken from meta-sedimentary rocks in the Stillwater contact aureole).

A large number of different dating methods have been attempted, with different rock and mineral types, which have resulted in a range of different reported ages (mainly 2600 to 2700 Ma) with widely varying precisions. An early study using the Rb-Sr isochron method on the surrounding hornfels yielded an age of 2692 +/- 45 Ma (Mueller and Wooden 1976) assuming that the Rb-Sr systematics of the hornfels were reset at the time of recrystallization. A Sm-Nd mineral isochron age of 2701+/- 8 Ma was determined for a gabbro from the Lower Banded Series (DePaolo and Wasserburg, 1979) and was considered to be one of the first precise age constraints from the Stillwater Complex. Study of chromitites using the Re-Os isotopic system,

with one sulfide-rich sample from the Basal Series and 14 samples from the Ultramafic Series, yielded an age of 2740 +/- 80 Ma (Lambert et al., 1989); the relatively large error may have been caused by hydrothermal alteration of olivine and amphibole and mobility of Re and Os. Nunes and Tilton (1971) provided the first U-Pb zircon date in the complex from a Stillwater chill zone, which yielded an age of 2725 +/- 25 Ma; this age was later revised to 2713 +/- 3 Ma (Nunes, 1981). The major problem with this result is that it is difficult to understand precisely what this sample represents (Wooden et al., 1991) as it could be interpreted as being part of the sill and dike suite that is located below the complex.

The most commonly accepted precise age determination of the Stillwater Complex is that of Premo et al. (1990), which is based on U-Pb zircon and baddelelyite dating by thermal ionization mass spectrometry (TIMS) (Premo et al., 1990). Premo et al. (1990) reported an age of 2705 ± 4 Ma, which is a composite age based on analyses of selected fractions (n=7) from two different samples in the Lower Banded Series. The age is based on discordant analyses and represents a 207Pb/206Pb upper intercept age along concordia.

Premo et al. (1990) also conducted a geochemical and geochronological study on the basal sill and dike suite, which is considered to represent the parent magma(s) for the Stillwater Complex. These rocks were divided into five compositional groups: gabbronorite, high-Mg gabbronorite, mafic norite, high-Ti norite, and olivine gabbro (Premo et al., 1990). U-Pb zircon dating yielded ages of 2711 ± 1 Ma for a group 1 gabbronorite, 2703 ± 10 Ma for a group 3 mafic norite, and 2712 ± 3 Ma for a group 4 high-Ti norite (Premo et al., 1990).

4.2 Geochronology of the Granophyres

Czamanske et al. (1991) reported some reconnaissance geochronological results as part of their study on the granophyres of the Stillwater Complex. Pb-isotope compositions were measured on five separate samples, including five whole rock samples and four plagioclase separates. Age ranges calculated from Pb-isotope relationships vary from 2125 to 2580 Ma (Czamanske et al., 1991), which is significantly younger than the accepted age of the Stillwater Complex. These younger ages are interpreted as being the result of a thermal event, no earlier than 2.1 Ga, that caused a re-equilibration of the Pb isotopic system in the granophyres (Czamanske et al., 1991). In addition, Czamanske et al. (1991) reported U-Pb zircon results for

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one sample. Five multi-grain fractions of zircon were analyzed with strongly discordant results that yielded a lower concordia intercept of 162 +/- 45 Ma and an upper concordia intercept of 2132 +/- 98 Ma, which is considered to be a minimum age (Czamanske et al., 1991). Most of the discordant analyses are located near the lower intercept and likely reflects a two-stage Pb-loss history that occurred after 2.1 Ga (Czamanske et al., 1991). Strong Pb-loss was likely related to the very high U and Th concentrations in the zircon grains, which would lead to massive radiation damage and metamictization resulting in preferential pathways for Pb-loss to occur. The upper intercept age of 2132 +/- 98 Ma likely reflects an event that caused Pb-loss younger than the crystallization age of the granophyres (Czamanske et al., 1991).

5.0 Petrology of the Granophyres

In this study, four granophyres (ST05-01, 06, 07 and 13) were sampled from three different stratigraphic locations in the Stillwater Complex (Figure 3). One of the sampling goals for this study was to ensure that there was at least one granophyre from each of the banded series (Figure 3). The samples were collected between July 23, 2005 and July 27, 2005 by Dr. James Scoates and Dr. Bill Meurer. All samples were collected in the field using a steel-headed sledgehammer. Prior to crushing for accessory phase minerals, representative hand samples were set aside from each sample (see Appendices) and polished thin sections were prepared for petrographic observation. Below, the main petrographic characteristics of each sample are summarized.



Figure 3. Location of the four granophyre samples with respect to major stratigraphic units within the Stillwater Complex.

5.1 Sample ST05-01

Sample ST05-01 was collected from the Upper Banded Series within the GN-III subzone (UTM coordinates: 0574166E/5034455N). The sample was located near the Picket Pin PGE zone (Figure 4c). Three thin sections were prepared from this sample (ST05-01A, B, C). This amphibole-bearing granophyre is a coarse-grained and homogeneous rock composed primarily of quartz (~25 vol%), K-feldspar (~30 vol%) and albite (~30 vol%) with minor amounts of amphibole, including hornblende and actinolite (~15 vol%). Overall, the texture of the sample is equigranular with a weak graphic texture developed within several K-feldspar grains (Figure 4A, 4B). There is abundant evidence for hydrothermal activity at some time after crystallization causing strong alteration of the K-feldspar grains. The K-feldspar grains (100-350 µm) have been almost completely altered to sericite and grain boundaries between neighbouring feldspar grains are difficult to distinguish. Quartz grains (200-300 µm in diameter) are mostly subhedral with a few euhedral grains present. Quartz exhibits strong undulatory extinction and sutured boundaries between quartz grains are common. The mafic minerals, such as hornblende and actinolite, typically form in clusters near quartz grains and have subhedral morphologies and range in size from 30-150 µm in diameter. Minor secondary chlorite is found in all of the thin sections, forming in patches in and along the edges of amphibole grains. Zircon, rutile and titanite occur in all thin sections of sample ST05-01.





Figure 4.A and B. Photomicrographs of entire petrographic thin sections (ST05-01A, ST05-01B) from the granophyre located near the Picket Pin PGE zone in the Upper Banded Series. Note the relative sizes and distribution of the main minerals (QTZ=quartz, AMPH=amphibole, SER=sericite). Both A and B are in crosspolarized light. C. Photograph of the field view of the outcrop showing the amphibole lined fractures. Coin is 2.75 cm in diameter. Photograph courtesy of Dr. James Scoates.

5.2 Sample ST05-06

Sample ST05-06 was collected from the Middle Banded Series within the AN-I zone (UTM coordinates: 0574258E/50321049N) (Figure 5C). The sample was taken from the massive granophyre "alaskite" body that was studied by Czamanske et al. (1991), which can exceed 200 metres in width. Two petrographic thin sections were prepared from this sample (ST05-06 A, B). The rock is coarse-grained and felsic, containing primarily quartz (~80 vol%) with moderate amounts of albite (~14 vol%), K-feldspar (~5 vol%), and rare mafic minerals present (~1 vol%). This sample has also undergone significant hydrothermal activity shown by extensive sericitic alteration of K-feldspar grains. The albite grains range between 200-1500 μ m in diameter and are approximately anhedral in morphology (Figure 5A, 5B). Quartz grains have been strongly deformed exhibiting sutured boundaries between grains, and contain internal fractures and strong undulatory extinction. Mafic minerals that are present include amphibole (actinolite), which occurs as small subhedral interstitial grains ranging from 20-40 μ m in diameter, and minor amounts of chlorite, which is associated with zones of high sericitic alteration and along actinolite boundaries. The texture of the sample is mostly equigranular, but some graphic intergrowths do occur. Zircon was found in both thin sections, as well as titanite.





Figure 5. A and B. Photomicrographs of entire petrographic thin sections (ST05-06A, ST05-06B) from the massive granophyre "alaskite" located in the AN-I zone within the Middle Banded Series. Note the relative sizes and distribution of the main minerals (QTZ=quartz, PLAG=plagioclase,). Both A and B are in cross-polarized light. C. Photograph of the field view of the outcrop showing the overall homogeneous texture found in this rock. Lens cap is 7.25 cm in diameter. Photograph courtesy of Dr. James Scoates.

5.3 Sample ST05-07

Sample ST05-07 (UTM: 0574327E/5031951N) was located at the contact between an anorthosite from the AN-I zone and the granophyre (alaskite) represented by sample ST05-06 (Figure 6C). The granophyre is coarse-grained and ranges in thickness from several centimeters up to 10 cm with large amphibole splays throughout the unit. Two petrographic thin sections were prepared from this sample (ST05-07 A, B). These thin sections can be sub-divided into two portions: a more felsic granophyre-like section and a heavily altered and mafic-dominated section.

The granophyre-like section is composed mainly of quartz (~40 vol%) and K-feldspar (~55 vol%) with minor plagioclase and amphibole. This sample exhibits a range of textures from graphic to equigranular with grains exhibiting subhedral morphology (Figure 6A, 6B). Quartz is present in two distinct forms. Quartz forms large anhedral grains, ranging in size from 100-300 µm in diameter, and shows strong undulatory extinction and internal fractures. Quartz also appears as finer grained clusters that occur in the spaces between larger feldspar and quartz grains. These grains show no evidence of fracturing or sutured boundaries and may represent a later stage of crystallization. There is moderate sericitic alteration of the feldspars, which results in a cloudy appearance of the grains in plane-polarized light, although twinning in the grains is still visible. Along fractures in quartz grains, fine-grained chlorite has filled the cracks and forms veins that connect between adjacent quartz grains.

The second section is composed predominantly of mafic minerals, especially actinolite (~40 vol%) and large amounts of alteration products such as chlorite (~50 vol%), with minor amounts of quartz and K-feldspar (~10 vol%). Actinolite grains are anhedral to subhedral and range from fine-grained interstitial fibrous clots to larger grains (~3 mm) that are equigranular to the quartz- and K-feldspar-dominated zone (Figure 6B). There are patches of sericite associated with the K-feldspar grains, which is most likely due to hydrothermal alteration. Chlorite occurs as an alteration product of mafic minerals, such as actinolite. Chlorite and forms patch-like regions throughout the sample and exhibits an anomalous blue colour in cross-polarized light. This part of the section contains only fine-grained intergrowths of actinolite, chlorite and sericite. Throughout these sections, titanite and zircon are also present.





Figure 6. A and B. Photomicrographs of entire petrographic thin section (ST05-07A) from the coarse-grained contact located between the massive granophyre (ST05-06) and a mafic cumulate within the Middle Banded Series. Note the relative sizes and distribution of the main minerals (QTZ=quartz, PLAG=plagioclase, SER=Sericite, AMPH=amphibole, Titanite). A, ordinary light; B, crosspolarized light. C. Photograph of the field view of the outcrop. Coin is 2.75 cm in diameter. Photograph courtesy of Dr. James Scoates.

5.4 Sample ST05-13

Sample ST05-13 was collected from the Lower Banded Series located near the base of the series within the N-I zone (UTM coordinates 0567460E/5033395N) (Figure 7C). The sample is an amphibole-bearing quartz- and K-feldspar-rich pegmatite, which forms the cores of mafic pegmatoids that cross-cut the basal part of the Lower Banded Series. Two petrographic thin sections were prepared for this sample (ST05-13 A, B). K-feldspar is the major constituent of the rock, comprising approximately 75 vol% of the rock, and has been almost completely altered to sericite. The two sections contain only a few very large (pegmatitic) K-feldspar grains, but due to the strong alteration the boundaries between the grains are indiscernible (Figure 7A, 7B). Quartz (10-15 vol%) is a minor component of this sample and exhibits an anhedral morphology and ranges in grain size from 1-10 mm in diameter. Quartz is unaltered compared to the K-feldspar grains and contains only minor undulatory extinction and internal fracturing. Carbonate is also present within these thin sections and shares coherent grain boundaries with minerals such as quartz and zircon, and comprises approximately 5-10 vol% of the thin sections.

Fine-grained epidote and actinolite grains are disseminated throughout the thin sections within the heavily sericitized K-feldspar. They are subhedral in morphology and range in size from 10-50 μ m in diameter with no preferred orientation. In ST05-13A, there is a large mafic grain between two large quartz grains that has been heavily altered and that may represent a former biotite grain. Chlorite is a major alteration product and is present as fine-grained laths that are oriented parallel to possible relict cleavage with dark green interference colours. Actinolite is a minor alteration product and is also oriented parallel to relict cleavage, but occurs as larger grains (~10-20 μ m). A bright red oxidized mineral is associated with zones of alteration forming web-like structures. Accessory phases, such as zircon, rutile, and titanite, occur within these thin sections.





Figure 7. A and B. Photomicrographs of the entire petrographic thin section (ST05-13A) from the pegmatitic granophyre within the Lower Banded Series. Note the relative sizes and distribution of the main minerals (QTZ=quartz, KSP=K-feldspar, SER=sericite, CHL=chlorite, EP=epidote). A, ordinary light; B, cross-polarized light. C. Photograph of the field view of the outcrop showing the pegmatitic texture found in this rock. Coin is 2.75 cm in diameter. Photograph courtesy of Dr. James Scoates.

6.0 U-bearing Accessory Minerals

Zircon, rutile and titanite were separated from the whole rock samples using conventional crushing, grinding, and Wilfley table techniques, followed by final concentration using heavy liquids and magnetic separation. All separation carried out by Hai Lin at the Pacific Centre for Isotopic and Geochemical Research. Mineral separation yielded abundant zircon (hundreds of grains) from all samples except ST05-07, abundant titanite (hundreds of grains) from all of the samples, and abundant rutile (hundreds of grains) from sample ST05-13 and minor amounts (tens of grains) from sample ST05-01. Single grains were handpicked by the author for examination for scanning electron microscopy (SEM) using back scattering electron imagery (BSE) and for U-Pb geochronology.

6.1 Zircon

Zircon occurs in all four of the granophyre samples. Zircon from sample ST05-01 occurs as interstitial grains (~50-150 μ m) associated with zones of mafic minerals such as hornblende (Figure 8A). From back-scattering imaging (BSE), the zircon grains have a very complex internal structure (Figure 9B). There is strong zoning between the outer and inner regions of the grains. Spot scan analysis by SEM of the outer, lighter zone yields a typical spectrum expected for zircon, whereas the inner zone shows a weak, but significant Ca-peak (Figure 10C). The zones that contain Ca appear to follow zones of higher metamictization that have undergone structural damage caused by self-irradiation (resulting from the decay of isotopes of U and Th to isotopes of Pb) (Geisler et al., 2007).

Zircon grains from sample ST05-06 are much smaller in size (~20-60 µm) and exhibit a more euhedral morphology, but show extensive internal fracturing. Zircon is found within K-feldspar grains, quartz grains and also intergrown at quartz-K-feldspar grain boundaries (Figure 8C, 8D). Zircon located in K-feldspar tends to be heavily metamict (Figure 8C) leaving almost no distinguishable features, whereas zircon within quartz grains appear pristine. Zircon intergrown with quartz and K-feldspar shares characteristics of the previous observations with more structural damage occurring adjacent to K-feldspar than to quartz (Figure 8D). The ST05-06 zircon grains also show evidence of strong internal fracturing and zoning within individual

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grains based on BSE imaging, again with noticeable Ca-peaks distributed throughout the grains (Figure 9C).



Figure 8. Photomicrographs showing the textural and mineralogical relationships of zircon from the granophyres. A. Photomicrograph (cross-polarized light) from sample ST05-01A. B. Photomicrograph (cross-polarized light) from sample ST05-07A. C and D. Photomicrograph (cross-polarized light) from sample ST05-06B. E. Photomicrograph (cross-polarized light) from sample ST05-07A. (QTZ=quartz, AMPH=amphibole, SER=sericite)



Figure 9. Scanning electron microscope (SEM) images using back scattering electron (BSE) imagery. A. Image of a euhedral zircon grain from sample ST06-07 showing growth zoning and no internal fractures. B. Image of a euhedral zircon grain from sample ST05-01 with dark grey zones containing Ca. C. Image of a strongly fractured zircon grain from sample ST05-06 that exhibits Ca-peaks. D. Image of a pristine interstitial zircon from sample ST05-13. E. Image of a titanite grain from sample ST05-13 with irregular grain boundaries. F. Image of a rutile grain from sample ST05-13 showing its uniform internal structure and irregular morphology.



Figure 10. A. Zircon grain from sample ST05-01. The lighter (brighter) area represents a zone of preserved zircon as there is no Ca-peak present. The darker areas have experienced stronger metamictization and have resulted in the introduction of Ca during fluid infiltration into the damaged crystal lattice. B. Spot scan analysis (intensity vs. wavelength) of the lighter zone. Note the absence of a Ca-peak. C. Spot scan analysis of the darker zone. Note the presence of a Ca-peak.

Zircon from sample ST05-07 (~30-100 μ m) occurs as interstitial grains located in large K-feldspar grains as well as within quartz grains. As with sample ST05-06, zircon located within quartz appears to have been shielded from fluid alteration and thus prevented further damage to the zircon crystal structure (Figure 8B, 8F). These grains seem to have a more intact internal structure compared to ST05-01 and 06 (Figure 11A) and show no evidence of Ca-peaks from spot scans.

Zircon in sample ST05-13 (~80-800 µm) occurs as interstitial grains with K-feldspar and is also contained within large grains of quartz and feldspar. Euhedral and prismatic grains are also visible in thin section and zircon shares grain boundaries with minerals such as calcite and quartz (Figure 8E). These more prismatic grains tend to be much smaller than the interstitial grains. From BSE imaging, zircon grains from ST05-13 has no resemblance to zircon from the other three samples (Figure 9D); as they exhibit anhedral morphology with no evidence of zoning within grains.

6.2 Titanite

Titanite is an accessory mineral in all four granophyre samples. Titanite occurs as large, elongated, equant to intergrown grains (~1-2.1 mm) associated with zones of strong alteration of K-feldspar grains to sericite and splays of fine-grained actinolite (Figure 11A, 11B, 11C, 11E, 11F). The titanite grains are typically broken with numerous internal fractures. Intergrown titanite grains are associated with large amphibole grains and form along grain boundaries (Figure 11D), they also tend to be smaller (~170 μ m) than the larger euhedral grains. Some of the titanite grains (especially those in sample ST06-06) are heavily metamict and have a cloudy appearance in plane-polarized light. SEM imaging of titanite grains reveals a structure with no evidence of zoning. Spot scan analyses indicate the presence of a small Al-peak within the crystal lattice.



Figure 11. Photomicrographs showing the textural and mineralogical relationships of titanite grains from the granophyres. A. Photomicrograph (cross-polarized light) from sample ST05-13B. B and C. Photomicrographs (plane-polarized light) from sample ST05-07A. D. Photomicrograph (cross-polarized light) from sample ST05-01C. E. Photomicrograph (plane-polarized light) from sample ST05-06B. F. Photomicrograph (cross-polarized light) from sample ST05-06A. (QTZ=quartz, AMPH=amphibole, CHL=chlorite)

6.3 Rutile

Rutile grains, which range in diameter from approximately 20-60 μ m, are found within samples ST05-01 and ST05-13, but are most abundant in sample ST05-13. They occur primarily as small irregular grains that are associated with zones of chloritic alteration of biotite or actinolite grains with no preference to relict cleavage (Figure 12). SEM imaging shows no zoning or inclusions within the rutile grains (Figure 9F).



Figure 12. Photomicrographs showing the textural and mineralogical relationships of rutile grains from samples ST05-01 and ST05-13. A. Photomicrograph (plane-polarized light) from sample ST05-01B. B, C, D, E, and F. Photomicrographs (all in cross-polarized light) from sample ST05-13A. (QTZ=quartz, CHL=chlorite, AMPH=amphibole, K-FSP=K-feldspar).

7.0 Analytical Methods

7.1 Zircon Treatment

Zircon grains from ST05-01 were mainly concentrated in the N2/M5 magnetic split, they have a distinct brownish red tint and are prismatic with little to no inclusions, but are highly fractured as noted in the previous section. ST05-06 contained a minor amount of zircon located in magnetic splits N2 and N2/M5. Zircon grains in ST05-06 are similar to the ones found in ST05-01, but are less prismatic, are moderately broken up and smaller in diameter. Very few zircon grains were found in any of the magnetic splits of ST05-07 and they are dark brown to opaque in colour and are heavily fragmented. A few grains were found of much smaller size, but were much clearer and have a light yellow colour and are more prismatic than the more metamict grains. Zircon grains from ST05-13 were abundant in the N2 magnetic split and all have a light pink colour, and exhibit a predominantly interstitial appearance; almost the entire N2 split was composed of zircon. In the more magnetic splits, the zircon grains tend to be more prismatic in shape, and also have a more opaque red colour.

All mineral treatment protocols and isotopic analyses were carried out at the Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia, Vancouver, Canada. Once zircon grains were selected, they were then transferred to quartz glass crucibles and annealed in a muffle furnace at 900°C for 60 hours before chemical abrasion. The chemical abrasion protocol at the PCIGR is described in Scoates and Friedman (2008) and the following description is adopted from this study with modifications. The principle behind the chemical abrasion technique (CA-ID-TIMS) is to completely remove the zircon domains that have lost Pb, which allows for the analysis of closed-system zircon grains (Mundil et al., 2004; Mattinson, 2005). Annealed grains were transferred into clean 10 mL Pyrex® beakers and moved to the clean lab for chemical abrasion. Samples were then agitated in 3N HNO₃ in an ultrasonic cleaner for 15 minutes, warmed to 60° +/- 10°C for 30 minutes, and then rinsed with ultrapure acetone and water.

A stepwise leaching approach was implemented for this study. The weight of each sample was made using aluminum weigh boats, which were teared on the scale before the grains were added. The grains were then added to the weigh boat and weighed again yielding the

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weight of the zircon grains. The samples were then placed into clean 3 mL Savillex screw-top vials that were fluxed in 6N HCl before use. To determine if all of the material was transferred, the weigh boat was put back onto the scale and the total weight of the sample was then corrected based on this measurement.

The first trial using chemical abrasion was implemented with zircon from sample ST05-01. The experiment involved using a full-strength HF mixture (50% HF + 1 part 8M HNO₃) and chemical abrasion (i.e. leaching) continued for 8 hours at 180°C. However, the zircon grains were so metamict that most of the material was removed from the crystal lattice during chemical abrasion. This left the grains so fragile that, when they were placed in the ultrasonic machine, they completely broke up and formed a powder. A solution of 10 parts 50% HF + 1 part 8M HNO₃ was mixed with 18 Ω H₂O at a 1:1 ratio. This was implemented due to the high-U content of these zircons grains. If there was no dilution of the HF solution then the zircons would most likely dissolve during chemical abrasion. 500 µL of this mixture was added to the Savillex vials and the lid was screwed on hand-tight. Vials were then transferred into Teflon liners stacked four high, and then 2.0 mL of the mixture, identical to the mixture in the 3 mL Savillex vials, was added to the Teflon liner to ensure equivalent vapour pressure inside and outside the sample vials (Mattinson, 2005). This is done to allow the vials to be tightened finger-tight so that the vials are in a closed system (Mattinson, 2005). These Teflon liners were then placed into bombs and placed into an oven. The samples started out at 80°C for 4 hours for the first leaching step and the temperature was increased by 20°C for the next two steps. After cooling, the samples from each leaching step were removed from the oven and the Teflon liner.

The leachate from inside the vials was pipetted out of the Savillex vials into a waste beaker, leaving behind the leached zircon grains. For sample ST05-01, the leachate was saved after every step to be analyzed on the mass spectrometer for U-Pb isotope ratios (due to time constraints, the leachates were not analyzed in this study). The vials were rinsed with acetone three times to remove any remaining possible leachate mixture, then HCl was added and the vial was put on a hot surface at 80°C for 20-30 minutes to allow them to flux. After fluxing, the HCl was removed and the vial was rinsed with acetone two more times before the 500 μ L of the diluted HF mixture was added to the vial for the next leach step. The acid strength of the mixture was increased to a 2:1 ratio of HF solution to pure water and the leaching step was repeated at 120°C. Zircon grains from samples ST05-06 and ST05-07 were removed from the leaching

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procedure after this step because the remaining grains that were not yet dissolved were heavily broken-up and several grains had dissolved during the last chemical abrasion step. The zircon grains from ST05-01 were then subjected to a final leaching step with the 2:1 mixture at 160°C for 4 hours. The zircon grains from sample ST05-13 were processed through this step, but were also treated with a full-strength HF mixture at 180°C for 8 hours (this was possible due to the pristine crystals found in this sample). The grains were then pipetted into clean 3.5 mL PFA Teflon® beakers and rinsed with ultrapure water; they were pipetted due to the delicate nature of the grains, because if they were transferred by means of tweezers, they likely would have disintegrated.

The single zircon grains were then transferred into clean 10 mL Pyrex® beakers with 2 mL of 6N HCl added to each beaker and warmed to 70°C for 30 minutes. The samples were then rinsed with acetone to ensure that no HCl remained in the beakers. The annealed, leached, and rinsed grains were then weighed and transferred to 300 μ L PFA microcapsules with one grain per capsule. A mixture of 50 μ L of 50 percent HF + 5 μ L of 14N HNO₃ was added to each beaker along with a ²³³⁻²³⁵U-²⁰⁵Pb isotopic tracer, and the beakers were capped and placed in a Teflon® liner. HF and nitric acids at a ratio of 10:1, respectively, were added inside the liner, then placed in a jacket and brought up to 240°C for 40 hours to allow the grains to completely dissolve. These solutions were then dried on a hotplate at 130°C. Finally, the fluorides were dissolved in 3.1 N HCl in the high-pressure metal jackets for 12 hours at 210°C.

Separation and purification of U and Pb utilized the ion exchange column chemistry techniques described by Parrish et al. (1987) where U and Pb are washed out one after the other into a single beaker. Leachates from sample ST05-01 were also spiked and followed the same procedures that the annealed and leached zircons went through. After column chemistry, however, they were transferred to clean 7 mL PFA beakers and dried after 2 μ L of 0.5N H₃PO₄ was added. As it was observed that these zircon grains can withstand chemical abrasion at a temperature of 160°C for 4 hours, another trial was done on grains from the three metamict samples, but the chemical abrasion steps began at 180°C for 4 hours. This was done because it was observed that the grains became increasingly broken-up as further steps were implemented. If the chemical abrasion began at a higher temperature range, but within a safe range where the grains may not dissolve, it would allow for the grains to be subjected to higher temperature leach

steps as they would not have been deteriorated from previous lower temperature leach steps. These grains however were relatively fragile after the first leaching step and when they were put on the hotplate in HCl to flux, they dissolved in the HCl.

7.2 Rutile Treatment

Rutile was found in samples ST05-01 and ST05-13. In ST05-01, minor rutile was found in the M5/N20 split, as well as in the N2/M5 magnetic split and range in colour from dark orange to amber. The grains range from rare euhedral to subhedral shapes and irregular fragments, and vary in size from 75 to 150 μ m. In contrast, ST05-13 had abundant dark red rutile in the N2 and the M5/N20 splits. Rutile grains range in shape from subhedral to mostly irregular fragments, and in size from 75 to 200 μ m.

Handpicked fractions of 10 to 11 grains were transferred into 10 mL Pyrex® beakers with a total of three fractions per sample. Roughly 2 mL of 1M HNO₃ was added to the beakers and allowed to flux on the hotplate for 30 minutes at 70°C, rinsed with ultrapure water and acetone, and then air-dried. The fractions were then weighed and transferred to 3.5 mL Savillex beakers and one mL of 50 percent HF + 14M HNO₃ was added along with a weighed drop of ²³³⁻ ²³⁵U-²⁰⁵Pb isotopic tracer. The beakers were then screwed closed and placed on the hotplate at 130°C for at least 48 hours. The rutile grains did not fully dissolve during the first step; there were still small fragments within the HF mixture, so a second dissolving step was used to completely dissolve the grains. The cap was then removed and the sample was dried at 130°C. One mL of 6.2N HCl was then added to the beakers and they were capped, placed on the hot plate and allowed to flux for 24 hours at 130°C. They were again uncapped, dried, and then one mL of 3.1 N HCl was added, and they were capped and placed on the hotplate again at 130°C for 24 hours.

Anion exchange procedures for rutile grains are similar to those for zircon, but have been slightly modified. Twice the volume of the anion exchange resin was used compared to the zircon protocol (0.5 mL). U was eluted into a beaker with 0.5 N HBr, followed by the washing of Pb into a separate beaker with 6.2N HCl. The U-fraction was then put on the hotplate at 110°C to almost complete dryness, then 1 mL of sub-boiled 6.2N HCl was added. The resin that was in the columns was rinsed with >18 Ω *cm water and conditioned in 6.2N HCl. The U solution was then

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reintroduced into the columns and rinsed with 8M HNO₃ to remove any iron that may be present. U was then washed out with water into the same beaker into which the Pb was washed into. The samples were then set on the hotplate to dry at which point 2 μ L of 0.5N H₃PO₄ was added.

7.3 Titanite Treatment

Titanite was abundant in magnetic split N20/M5 for sample ST05-01. The grains ranged in colour from almost clear to a pale-yellow colour. All grains exhibited subhedral morphology and ranged in size from 100 to 200 μ m. Titanite grains from sample ST05-06 were abundant in magnetic split N20/M5. They were mainly pale-yellow and exhibited a subhedral morphology (75 to 150 μ m) with a minor amount of the grains being irregular and fragmented. Titanite from ST05-07 was minor in magnetic split N20/M5 and was found mainly in the N5/M2 split. The grains were mainly a pale-yellow colour and were irregular fragments ranging in size from 150 to 200 μ m. Titanite from sample ST05-13 was abundant in numerous magnetic splits (N2, M2/N5, N20/M5). They were mainly pale-yellow in colour with subhedral morphology (and rare euhedral grains) and ranged in size from 150 to 200 μ m. Processing of the titanite grains followed the same procedures as those described for the rutile grains.

7.4 Isotope Analysis

After chemical processing, all zircon, rutile, and titanite samples were loaded onto single zone-refined Re filaments with 5μ L of silicic acid activator (Gerstenberger and Haase, 1997). Isotopic ratios were measured using a modified single-collector VG-54R thermal ionization mass spectrometer equipped with a Daly photomultiplier housed at the Pacific Centre for Isotopic and Geochemical Research (Table 3). The analytical conditions are similar to those outlined in Scoates and Friedman (2008). Measurements were done in peak-switching mode on the Daly detector. U and Pb total procedural blanks were 0.2 pg and 0.5-2 pg for zircon, respectively, and 0.8 pg (±50%) and 8 pg (±40%) for rutile and titanite, respectively (Table 3). U fractionation was determined directly on individual runs using the ²³³⁻²³⁵U tracer. Pb isotope ratios were corrected for a fractionation of 0.23%/amu ± 40% based on replicate analysis of the NBS-982 Pb reference material throughout the course of this study (Table 3). The UBC ²³³⁻²³⁵U-²⁰⁵Pb isotopic tracer

was calibrated in 2003 against mixed reference solutions prepared in-house from standard references (NBS 982) and uranium (CRM 112-A; natural composition U metal, formerly NBS 960) (Scoates and Friedman, 2008). Calibration results for two reference solutions of different U/Pb ratios yielded indistinguishable results. During 2005, the original calibration was checked against three mixed U-Pb gravimetric reference solutions from MIT, UC Santa Barbara, and NIGL (UK) made available through the EARTHTIME initiative (http://www.earth-time.org) and gave a U/Pb ratio that agreed to more than 0.1% of the 2003 value. All analytical errors were numerically propagated through the entire age calculation using the technique of Roddick (1987). Standard Concordia diagrams were constructed and U-Pb Concordia ages calculated with Isoplot 3.00 (Ludwig, 2000); all errors are quoted at the 2σ level. All isotopic analyses, including ID-TIMS and data reduction, were carried out by Dr. Richard Friedman at the PCIGR.

Table 3	dd-U	TIMS a	malytics	al data 1	or zire		m me :	StillWater Con	uptex	6.10		e, 10			11	
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	(E)	(udd)	(udd)	R.	ž	(Bd		²⁰⁶ Pb/ ²³⁸ U	207 _{Pb} /235U	²⁰⁷ Pb/ ²⁰⁶ Pb	coef.	discordant	²⁰⁶ Pb/ ²³⁸ U	207 _{Pb} /235U	²⁰⁷ Pb/ ²⁰⁶ Pb	
ST 05-0	1															
A, 2	*s	289.9	131.1	8017	150.1	4.7	0.244	0.42295 ± 0.08	8 10.2108 ± 0.1	1 0.17510 ± 0.05	0.937	15.1	2273.8 ± 3.1	2454.1±2.1	2607.0 ± 1.6/1.6	
B, 2	*	348.1	166.2	5786	111.4	13.4	0.201	0.45009 ± 0.12	2 11.0467 ± 0.1	5 0.17801 ± 0.05	0.940	10.8	2395.7 ± 4.8	2527.1 ± 2.7	$2634.4 \pm 1.8/1.8$	
0	8	348.2	140.9	12720	232.1	2.0	0.177	0.38351 ± 0.07	7 9.4233 ± 0.10	0.17821 ± 0.05	0.874	24.1	2092.6 ± 2.3	2380.1 ± 1.8	$2636.3 \pm 1.8/1.8$	
р	4*	319.3	157.3	26090	466.3	1.4	0.189	0.46483 ± 0.06	5 11.4956 ± 0.10	0.17937 ± 0.05	0.940	8.5	2460.8 ± 2.6	2564.2 ± 1.9	2647.0 ± 1.6/1.6	
E, 2	10*	158.5	46.9	13980	253.5	2.0	0.164	0.28232 ± 0.07	7 6.7174 ± 0.10	0.17257 ± 0.05	0.940	42.7	1603.1 ± 1.9	2074.9 ± 1.8	2582.7 ± 1.6/1.6	
Ĕ4	* 5	553.9	256.0	20680	376.4	3.6	0.196	0.43677 ± 0.06	5 10.6025 ± 0.10	0.17606 ± 0.05	0.940	12.7	2336.2 ± 2.4	2488.9 ± 1.9	$2616.1 \pm 1.6/1.6$	
Д, 6	64.9	52.5	35.4	17940	405.5	5.8	1291	0.50692 ± 0.07	12.9887 ± 0.10	0.18584 ± 0.05	0.928	2.8	2643.4 ± 3.0	2678.8 ± 2.0	2705.7 ± 1.6/1.6	
12.6	66.0	67.9	23.3	4662	106.3	152	1360	0.26340 ± 0.11	4.2666 ± 0.1	4 0.11748 ± 0.06	0.933	24.0	1507.2 ± 3.0	1687.0 ± 2.3	$1918.2 \pm 2.0/2.0$	
5.E	75.9	55.3	38.4	2986	74.8	43.5	1551	0.49948 ± 0.09	9 12.5431 ± 0.1	2 0.18213 ± 0.07	0.802	2.8	2611.6 ± 3.7	2646.0 ± 2.2	2672.4 ± 2.3/2.3	
9 FL	5.95	94.5	6.7	6372	149.6	2.1.5	1 248	0.50316 + 0.06	12,8291 + 0.10	0 0 18492.+ 0 05	0 931	5.5	26274+2.4	2667 2.+1 9	2,697 5 + 1 7/1 7	
0	40.0	516	15.6	185	8	0 000	0374	0.51173 ± 0.14	12 9907 ± 0.50	CF 0 7 11841 0 0	0100	1 -	2664.0 ± 6.0	7678 9 4 9 4	2690.2 ± 13.7/13.8	
2 1 1 2	0.02	200	0.01			210			10 I 002011 3	74'0 E 11401'0 0		1 0 2		1/2 T C 0/0/2 C	0.01/01 E 7/0207	
R4. 7	96.6	5.46	62.7	872	149.6	215	1248	0.50316 ± 0.06	112.8291 ± 0.10	0.18492±0.05	0.931	3.2	2627.4 ± 2.4	2667.2 ± 1.9	2697.5 ± 1.7/1.7	
ST 05-0	9															
A	;*	87.3	4.6	76	1.2	42	0.567	0.04735 ± 0.83	0.9418 ± 1.83	0.14426 ± 1.42	0.661	88.8	298.2 ± 4.8	673.8 ± 18.0	2279.0 ± 48.2/49.8	
щ	÷5	805.0	50.3	2153	42.1	6.5	0.505	0.05661 ± 0.07	1.0819 ± 0.12	0.13861 ± 0.06	0.889	86.2	355.0 ± 0.5	744.6 ± 1.3	2209.9 ± 2.2/2.2	
0	\$	1205.9	86.7	3859	75.3	63	0.437	0.06557 ± 0.06	1.3650 ± 0.10	0.15097 ± 0.05	0.937	85.1	409.4 ± 0.5	874.0 ± 1.2	2357.0 ± 1.8/1.8	
11. 8	53.1	58.0	28.2	6862	139.1		0.667	0.41259 ± 0.08	10.3892 ± 0.11	0.18263 ± 0.05	0.922	19.8	2226.8 ± 2.9	2470.1±2.1	2676.9 ± 1.7/1.7	
14 4	30.7	449	26.8	3854	L L L	010	0.649	0.50865 ± 0.08	12.9644 + 0.11	0 18486 + 0 06	0.890	2.1	26509+34	2677 1 + 2.1	26969 ± 1 8/1 8	
	2	Ì				2					200					
ST 05-0	Ŀ															
A, 2	10*	541.8	123.5	12520	231.0	5.9	0.216	0.21883 ± 0.07	4.52736 ± 0.11	0.15005 ± 0.05	0.937	50.2	1275.7 ± 1.6	1736.0 ± 1.8	2346.5 ± 1.6/1.6	
м	10*	755.7	269.9	15150	299.3	10.0	0.421	0.32593 ± 0.07	6.97263 ± 0.11	0.15516 ± 0.05	0.937	27.9	1818.6 ± 2.2	2108.0 ± 1.9	2403.6 ± 1.6/1.6	
c C	2 *	1438.2	201.5	25590	433.8	2.4	0.136	0.13711 ± 0.07	2.83427 ± 0.10	0.14993 ± 0.05	0.913	68.8	828.3 ± 1.1	1364.7 ± 1.6	$2345.1 \pm 1.7/1.7$	
р	2 *	333.3	92.9	12670	215.9	22	0.165	0.26855 ± 0.05	5.97452 ± 0.10	0.16135 ± 0.05	0.955	42.5	1533.4 ± 1.5	1972.1 ± 1.7	$2469.9 \pm 1.6/1.6$	
щ	5 *	712.9	101.5	237.6	4.3	54.4	0.112	0.13844 ± 0.28	3.13418 ± 0.79	0.16419 ± 0.62	0.709	70.8	835.8 ± 4.3	1441.1 ± 12.1	2499.3 ± 20.8/21.1	
13°8	102.1	159.4	26.3	3122	60.3	48.9	0.339	0.15491 ± 0.08	3.07754 ± 0.12	0.14409 ± 0.06	0.912	63.4	928.4 ± 1.4	1427.1 ± 1.8	2276.9 ± 2.0/2.0	
ST 05-1	3															
A	14.0	74.0	45.7	13920	273	2.4	0.679	0.52200 ± 0.07	13.4033 ± 0.11	0.18623 ± 0.05	0.932	0.1	2707.7 ± 3.0	2708.5 ± 2.0	2709.1 ± 1.6/1.6	
щ	18.5	146.9	90.4	74420	1452	12	0.657	0.52278 ± 0.06	13.4282 ± 0.10	0.18629 ± 0.05	0.946	-0.1	2710.2 1.9	2709.7 ± 1.5	2709.7 ± 1.5/1.5	
c C	18.8	237.1	148.1	51030	1078	2.8	0.732	0.52254 ± 0.13	13.4178 ± 0.15	0.18624 ± 0.05	0.952	0.0	2709.5 2.9	2709.2 ± 1.6	2709.2 ± 1.6/1.6	
ы	13.0	116.4	208.0	67640	1367	0.7	0.728	0.52248 ± 0.09	13.4283 ± 0.12	0.18640 ± 0.12	0.904	0.0	2709.7 ± 3.9	2710.3 ± 2.2	$2710.7 \pm 1.7/1.7$	
Ē4	22.9	76.2	45.8	15180	322.6	3.7	0.612	0.51446 ± 0.11	13.1977 ± 0.14	0.18606 ± 0.05	0.944	1.4	2675.7 ± 4.8	2693.9 ± 2.6	2707.6 ± 1.6/1.6	
11, 5 2, 5	44.8	393.1	142.9	1575	33.0	221.0	0.562	0.31774 ± 0.07	7.55321 ± 0.12	0.17241 ± 0.07	0.885	35.5	1778.7 ± 2.0	2179.3 ± 2.2	$2581.2 \pm 2.4/2.4$	
В, 5	103.5	64.4	7.0	1042	21.1	37.4	0.485	0.09553 ± 0.07	2.42699 ± 0.13	0.18426 ± 0.08	0.841	81.6	588.2 ± 0.8	1250.6 ± 1.9	2691.6 ± 2.7/2.7	
1 A, B, e	tc are zi	ircon gra	tins that	underw	ent CA SE2 ul	A pre-ti tra-mi	reatment	t; T1, T2: titanit	te, R1, R2: rutil	e. Numeral follo	wing co	mma: num baudowad	ber of grains i to + 1 micro	f more than 1.		
2. Correc	ted for	snike hl	u ou sa ank (0.2	no (zin	m 7776	uur-en 10.8	uno (titar	ite rutile) + 50	10gram, 01 whe	at uctioned by . , c nd mass fractionat	ion wh	ich is direc	tlv determined	giailt. 1 with 23311-23	511 snike	
4. Radios	zenic Pt	correc	ted for s	nike. fra	actiona	tion. b	lank and	d initial commo	on Pb. Mass frac	ctionation correcti	on of 0.	23% /amu	± 40% (2 sign	na) is based on	analysis of NBS-982	
Ph refere	nce mat	terial thr	onshout	t course	of stuc	N. BI	ank Ph s	nd of 0.5-2 no	for zircon) and	8 ng for titanite a	nd rutil	e + 40% (2	sioma) with (comnosition of	206Ph/204Ph =	
18.50 ± 2	?%; 207	Pb/204F	b = 15.5	$50 \pm 2\%$: 208P	b/2041	Pb = 36.	$40 \pm 2\%$ (zircor	n) and 206Pb/20	$04Pb = 17.23 \pm 2^{\circ}$	%: 207P	b/204Pb =	$15.08 \pm 2\%$; 2	208Pb/204Pb =	$36.04 \pm 2\%$, all at 2	

5. Measured ratio corrected for spike and fractionation.
5. Measured ratio corrected for spike and fractionation.
6. Ratio of radiogenic to common Pb.
7. Total weight of common Pb.
8. Model Th/U ratio calculated from radiogenic 208Pb/206Pb ratio and 207Pb/206Pb age.
9. Corrected for spike, fractionation, blank isotopic composition.
10. % discordance to origin.
11. Age calculations are based on decay constants of Jaffey et al., 1971.

8.0 Results

8.1 Sample ST05-01

For sample ST05-01, isotope ratios for chemically annealed and abraded single grains of zircon (n=6) were analyzed by ID-TIMS (Table 3). U-Pb data for all six grains are strongly discordant (8.5 to 42.7%) and yield a range of 207 Pb/²⁰⁶Pb dates from 2583 to 2647 Ma (Figure 13A). It is not possible to calculate a statistically viable regression line for these analyses that gives a low-MSWD. For titanite, the analysis of four multigrain (n=5-6) fractions yields less disconcordant results (2.8 to 24%) with a range of 207 Pb/²⁰⁶Pb ages from 1918 to 2706 Ma. Again, a statistically viable regression line cannot be calculated that includes all four titanite results that would yield a low-MSWD. The analyses of three rutile fractions yielded results similar to those for titanite (1.2 to 5.8% discordance; 207 Pb/²⁰⁶Pb dates from 2657 to 2697 Ma).

8.2 Sample ST05-06

For Sample ST05-06, isotope ratios of chemically annealed and abraded singe grains of zircon (n=3) yielded U-Pb data that are strongly discordant (85 to 88%) with a range of 207 Pb/ 206 Pb ages from 2210 to 2357 Ma (Figure 14). The results for the two titanite fractions (4 and 8 grains each) for sample ST05-06 are less discordant (2.1-19%) and yield a two-point regression line with a lower concordia intercept of 214 ± 23 Ma and an upper concordia intercept 2698.8 ± 2.0 Ma (2σ , including tracer calibration, decay-constant errors not included; MSWD = 0.00). The upper intercept age could be interpreted as the time when the rock cooled below the closure temperature for Pb diffusion in titanite (~650-700°C; Cherniak, 1993). However, two-point isochrons are of dubious quality and a rigorous assessment of the titanite age from sample ST05-06 will require additional analyses.



Figure 13. Concordia diagrams for the analytical results of zircon, rutile and titanite from ST05-01. A. The relative positions of all three U-Pb accessory phases are indicated and illustrates the discordance of the annealed and chemically abraded zircon grains. B. An expanded view of the relative positions of the titanite and rutile results. The labels beside the ellipses correspond to grain identifiers in the first column of Table 3. The numbers along Concordia indicate age in millions of years (Ma).



Figure 14. Concordia plots for the analytical results of zircon and titanite from ST05-06. A. Results for the annealed and chemically abraded zircon grains. B. Results from the two titanite fractions with a calculated regression line (uncertainty is reported in 2σ values, including tracer calibration errors; decay-consant errors are included for the error in square brackets). The labels beside the ellipses correspond to grain indentifiers in the first column of Table 3.

8.3 Sample ST05-07

For sample ST05-07, the isotope ratios for chemically annealed and chemically abraded single grains of zircon (n=5) are strongly discordant (28 to 71%) and yield a range of 207 Pb/ 206 Pb ages from 2346 to 2499 Ma (Figure 15). The results for a multigrain fraction (n=8) of titanite is also strongly discordant (63%) with a 207 Pb/ 206 Pb age of 2277 Ma. Due to the strong discordance of all analyses, no age interpretation is possible for this sample.

8.4 Sample ST05-13

Samples ST05-13 was the only granophyre sample that yielded concordant analytical results for zircon. The U-Pb data for chemically annealed and abraded single grains of zircon (n=4) are concordant to slightly discordant (0-1.4%) and the result of a poor U-Pb analysis for a single grain is slightly reversely concordant (-0.1%). The U-Pb Concordia age for the first group of results is 2709.60 \pm 0.80 Ma (2 σ , including tracer calibration, decay-constant errors not included) (MSWD = 0.052, probability = 0.82), which is interpreted as the age of crystallization for this granophyric rock assuming that the closure temperature for Pb diffusion in zircon is greater than 950°C (Cherniak and Watson, 200). When the decay-constant errors are included in the calculations, the concordia age is 2709.7 \pm 2.6 Ma (2 σ) (MSWD = 0.0013, probability = 0.97). A weighted mean ²⁰⁷Pb/²⁰⁶Pb age for the four concordant results is 2709.7 \pm 0.8 Ma, which is consistent with the concordia age (Figure 16). The results for the two multigrain (n=5) titanite fractions are strongly discordant (35 to 82%) and yield a range of ²⁰⁷Pb/²⁰⁶Pb ages from 2581 to 2692 Ma.



Figure 15. Concordia diagram showing the analytical results of chemically annealed and abraded single grains of zircon (n=5) and a multigrain fraction (n=8) of titanite. The labels beside the ellipses correspond to grain identifiers in the first column of Table 3.



Figure 16. U-Pb analytical results for zircon from sample ST05-13. A. Results from annealed and chemically abraded zircon grains (n=4) showing the calculated U-Pb Concordia age (uncertainty reported as 2σ , including tracer calibration errors; decay constant errors are not included). B. Plot showing the weighted mean 207 Pb/ 206 Pb age based on the results of four single grains of zircon (error bars are presented in 2σ).

9.0 Discussion

9.1 The role of metamictization on U-Pb systematics of zircon in the Stillwater granophyres

The melts from which the granophyres in the Stillwater Complex crystallized were latestage and strongly fractionated, which produced zircon grains with high U-contents (i.e. U is typically highly incompatible element). Three of the four granophyre samples examined in this study contained zircon with moderate to very high-U contents: ST05-01 (156 to 554 ppm), ST05-06 (87 to 1206 ppm) and ST05-07 (333 to 1438 ppm). The zircon grains from these three samples are dark brown and show complex internal structures indicative of a degree of damage due to the effects of radioactive decay. The zircon grains in sample ST05-13 have lower U concentrations (74 to 237 ppm) compared to the other samples. The high-U contents and associated structural damage by self-irradiation (metamictization) over 2.7 billion years allowed for substantial Pb-loss since their crystallization. Zircon grains that have experienced strong damage to their crystal lattice leave preferential pathways for fluid to migrate inwards, which in this case of the Stillwater Complex may be related to a fluid or metamorphic event. Based on the resetting of Pb-Pb isotope systematics of sulfides of the Lower Banded Series, fluid mobilization likely occurred at ca. 1.7 Ga (McCallum et al. 1999). This hydrothermal activity may have caused additional alteration to the structure of zircon and Pb-loss, and may have created pathways for diffusion to occur thus allowing for even more Pb-loss (e.g. Geisler et al., 2007). Episodic Pb-loss is expressed in the analytical results of these single zircon grains by strong discordance (8.5 to 89%) and a wide range of 207 Pb/ 206 Pb ages for grains from individual samples (from 2210 to 2647 Ma).

The chemical annealing and abrasion technique was specifically designed to eliminate the effects of Pb-loss by annealing structurally damaged areas of the grains and selectively acid-leaching higher U-content zones (Mundil et al., 2004; Mattinson, 2005). However, all results for zircon from these three samples (ST05-01, ST05-06, ST05-07) are strongly discordant even after annealing and leaching. This indicates that the grains were too damaged by self-irradiation and likely experienced several episodes of Pb-loss since crystallization. If there was only one event causing Pb-loss then the results from all of the grains should be displaced from concordia and define a single regression line with a lower intercept correlating to the age of the Pb-loss event.

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Episodic Pb-loss appears to also have occurred in titanite and rutile grains from all four granophyre samples in this study, with the possible exception of titanite from sample ST05-06, where additional analyses are required to refine the preliminary 2-point 207 Pb/ 206 Pb upper intercept age of 2698.8 ± 2.0 Ma.

9.2 Implications for the crystallization age of the Stillwater Complex

The interpreted crystallization age of the granophyre from the Lower Banded Series (ST05-13) is 2709.60 \pm 0.80 Ma. This is the most precise date determined for a rock from the Stillwater Complex and the only one to be based on concordant U-Pb results. As the granophyres are cross-cutting bodies, this result places a minimum age on the crystallization of the Lower Banded Series. This age is just within error of the combined zircon/baddeleyite age of 2705 \pm 4 Ma from Premo et al. (1990). The age of the granophyre is consistent with the U-Pb ages of the associated sill and dike suite which are mostly in the range from 2010 to 2012 Ma. (Figure 17). Based on thermal modelling constraints, emplacement, crystallizing and cooling of the Stillwater Complex may have occurred in a relatively short period of time (29,000 to 1 million years) (Selkin et al., 2008). The preliminary results of this study suggest that the crystallization age of the Stillwater Complex, from the early sill and dike suite to the late granophyres, is likely ca. 2010 Ma.



Figure 17. Diagram comparing precise radiometric age determinations for the Stillwater Complex and related rock units. A indicates the Sm-Nd age retrieved from DePaolo and Wasserburg (1979); B indicates the U-Pb zircon age from Nunes (1981); all other ages except for the one labelled ST05-13 are from Premo et al. (1990). Sample ST05-13 is the age of the granophyre from this study.

10.0 Conclusions

This study on the U-Pb geochronology of granophyres from the Stillwater Complex in southwest Montana (USA) yields the following conclusions:

- 1. The granophyres are late-stage bodies that intrude layered cumulate rocks of the complex and contain abundant U-bearing accessory minerals (zircon, titanite, and rutile).
- 2. Zircon in three of the granophyre samples is partially to strongly metamict, resulting in a dark-brown discolouration, structural damage, incorporation of Ca during fluid infiltration, and strongly discordant U-Pb results.
- Episodic Pb-loss occurred in zircon grains in samples ST05-01, ST05-06 and ST05-07 and reflects a complex geological history possibly related to a major fluid infiltration event at 1.7 Ga.
- 4. The effects of chemical abrasion on highly metamict, high-U zircon grains may not be sufficient to remove all of the radiation damage to the crystal lattice to produce concordant or near concordant results.
- 5. Titanite and rutile grains from sample ST05-01, ST05-06, and ST05-07 have also experienced minor to significant Pb-loss.
- 6. A precise U-Pb concordia age of 2709.60 ± 0.80 Ma was determined from a pegmatitic clot in a mafic pegmatoid from the Lower Banded Series and is interpreted as the crystallization age of this granophyre.

11.0 Suggestions for Future Work

Although a precise date has been determined for the crystallization age of a single granophyre in the Stillwater Complex, further study is needed to constrain the duration of emplacement and the crystallization of the complex and its cooling history. Clearer, less metamict zircon grains were picked form the three samples that yielded the strongly discordant U-Pb data, but they could not be processed and analyzed in the timeframe of this thesis. These grains will be annealed and leached at the same temperature and duration as the last "failed" leach, but they will not be fluxed in HCl after leaching. Clear sectors of these zircon grains will

then be broken off of the remaining zircon after leaching for analysis. This should allow for more concordant ages to be produced and aid in establishing precise crystallization ages for these samples. Additional titanite fractions should be analyzed for all four samples and careful inspection of the microcapsules must be conducted after complete dissolution to ensure that all of the material has dissolved. The titanite grains should be subjected to the same conditions as zircon using full-strength HF in microcapsules to ensure full dissolution. Rutile from samples ST05-01 and ST05-13 should also be subjected to the same conditions as zircon to ensure complete dissolution. Finally, the leachates from the stepwise leaching experiments of sample ST05-01 should be analyzed for their U-Pb isotopic systematics to provide additional constraints on the effect of leaching of these high-U zircon grains and implications for CA-ID-TIMS U-Pb geochronology.

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Appendix 1. Photographs of representative hand sample specimens of Sample ST05-01. (coin is 1.8 cm in diameter).



Appendix 2. Photograph of representative hand sample specimens of Sample ST05-06. (coin is 1.8 cm in diameter).



Appendix 3. Photograph of representative hand sample specimens of Sample ST05-07. (coin is 1.8 cm in diameter).



Appendix 4. Photograph of representative hand sample specimens of Sample ST05-13. (coin is 1.8 cm in diameter).

