

Age of the Stillwater Complex

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The Archean Stillwater Complex, a large mafic-ultramafic layered intrusion in the Beartooth Mountains of Montana (USA) and host to the world-class J-M Reef platinum group element deposit [1], may represent a sub-volcanic reservoir through which a substantial quantity of magma was processed [2]. We present U-Pb ID-TIMS results for ultramafic, mafic, and felsic samples from across the exposed max. 8 km-thick intrusion to constrain the age and duration of magmatism associated with this major intrusion. The accepted age for plagioclase-rich rocks of the Banded Series is ca. 2704 Ma with older ages recorded in the basal sills and dikes (2710-2713 Ma) [3]. Our U-Pb results for three mafic samples reveal a small range of weighted ²⁰⁷Pb/²⁰⁶Pb ages at ca. 2709 Ma, which we interpret as the age of crystallization of the Banded Series: 2708.80 ± 0.75 Ma (baddeleyite) and 2709.05 ± 0.85 Ma (zircon) for a troctolite from the J-M Reef package in the Lower Banded Series, and 2708.70 ± 0.82 Ma (zircon) for an olivine gabbro in the OB3 Zone and 2709.82 ± 0.51 Ma (zircon) for anorthosite from the AN2 Zone of the Middle Banded Series. A preliminary age of 2710.7 ± 1.1 Ma for high Th/U (8-14) zircon from a feldspathic orthopyroxenite at the top of the Bronzite Zone suggests that the lower Ultramafic Series could be resolvable older than the overlying Banded Series.

Small-volume granophyric and pegmatitic rocks are found throughout the Banded Series and some may represent extreme differentiates [4]. Samples studied include a pegmatitic ksp-qtz core to a gabbroic pegmatoid in the Lower Banded Series (N1 Zone), an alaskite (quartz diorite) and an amphibole-rich reaction zone between the alaskite and anorthosite (AN1 Zone) in the Middle Banded Series, and an amphibole-bearing granophyre from the Upper Banded Series (GN3 Zone). U-Pb dating of zircon from the N1 pegmatite yields a weighted ²⁰⁷Pb/²⁰⁶Pb age of 2709.65 ± 0.80 Ma, which is identical to ages from the dated mafic rocks. Zircon grains from the other three samples are strongly metamict and U-Pb results are strongly discordant (12-86%). Stepwise leaching experiments on the GN3 granophyre reveal two distinct Pb-loss events at ca. 2.0 Ga (leachates) and 2.7 Ga (residues). Titanite ages from the pegmatite and the alaskite agree with the U-Pb zircon ages from the mafic rocks (ca. 2708-2709 Ma), whereas titanite from the other two samples exhibits a wide range of discordance (1.5-61%) suggesting multiple stages of Pb-loss. The disturbed titanite U-Pb systematics and identified Pb-loss events reflect the combined thermal and alteration effects produced by a wide range of post-crystallization events, including the emplacement of a regionally extensive granitic batholith (Mouat quartz monzonite), multiple generations of mafic dike swarms, and greenschist facies metamorphism.

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Tc(IV) complexation with organic ligands - an overview

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Introduction

⁹⁹Tc represents a significant environmental contaminant because of its long half-life of 2.1·10⁵ y, complex chemistry, and potential high mobility. Although the anionic and highly mobile Tc(VII) is stable under oxic environments, it can be reduced to the sparingly soluble Tc(IV) and reductive precipitation of Tc has been proposed as one of the promising remedial approaches to impede Tc migration offsite. However, at environmentally relevant pH Tc(IV) forms cationic and neutral species, which can complex to soluble organic ligands and induce Tc(IV) solubilization. It is therefore necessary to assess Tc(IV) complexation with relevant organic ligands, including ligands commonly found in nuclear wastes (e.g. EDTA) and those ubiquitous in the environment (e.g. humic acids).

Results and conclusions

The stability constants of Tc(IV) with acetate, citrate, EDTA, and a variety of humic acids were experimentally determined using a solvent extraction method – a summary of these stability constants is presented in **Table 1**. Additionally, the influence of selected organic ligands (EDTA and humic acids) on Tc(IV) solubility was experimentally measured [6]. The addition of 2.5 mM EDTA leads to an increase of Tc(IV) solubility by over two folds, reaching a Tc(IV) concentration of 4·10⁻⁷ M at pH 6, in good agreement with modeling calculations performed based on the EDTA stability constants, which predicts a Tc(IV) solubility of 4.6·10⁻⁷ M in presence of the same EDTA concentration and at same pH.

Acetate	$\log\beta^0_{1,-1,1} = 2.8 \pm 0.3$	I = 0 M	[1]
Oxalate	$\log\beta^0_{1,0,1} = 7.2 \pm 0.2$	I = 0 M	[2]
Citrate	$\log\beta^0_{1,-1,1} = 7.5 \pm 0.2$	I = 0 M	[3]
Humic acid	$\log\beta_{1,-1,1} = 6.2 \pm 0.6$	I = 0.1 M	[4]
EDTA	$\log\beta^0_{1,0,1} = 20.0 \pm 0.4$	I = 0 M	[5]
	$\log\beta^0_{1,1,1} = 25.3 \pm 0.5$	I = 0 M	

Table 1: Stability constants of Tc(IV) complexes with different organic ligands.

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[5] Boggs *et al.* (2011) *Radiochimica Acta* Accepted.

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