Age of the Bushveld Complex

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Determining the precise age of the Bushveld Complex, the world's largest layered intrusion located in the northern Kaapvaal craton of South Africa, has been a longstanding problem. The age and duration of magmatism associated with the complex is critical for establishing the genetic relations among its different rock units (Rustenburg Layered Suite, overlying Rooiberg Group felsic volcanic rocks, intrusive Rashoop Granophyres) and timing of formation of its world-class ore deposits (Cr-PGE-V). We report chemical abrasion ID-TIMS U-Pb zircon results (all ages reported as weighted $^{207}Pb/^{206}Pb$ averages) for 8 samples from the layered mafic rocks of the complex and the roof. These results demonstrate that the Bushveld Complex spans an ~7 million year interval from 2061 to 2054 Ma with major magma emplacement at ca. 2060 and 2055 Ma. In the mafic rocks of the Rustenburg Layered Suite, the ages overlap within analytical uncertainty at ca. 2055-2056 Ma for a diorite from the top of the Upper Zone ~50 m below the roof (2056.52 ± 0.81 Ma) and for two samples, ~300 km apart in the Western and Eastern limbs, from the PGE-rich Merensky Reef at the top of the Upper Critical Zone (2055.30 ± 0.61 Ma; 2056.13 ± 0.70 Ma, revised from [1]). These results are consistent with rapid filling, crystallization, and cooling of the upper 2/3 of the intrusion [2]. Ages for felsic rocks in the roof above the level of the Upper Zone diorite in the Eastern Limb range from 2054-2056 Ma, including a granodiorite mixed with hornfels or "leptite" (2054.83 ± 0.86 Ma), a granophyre from the Rashoop Granophyre Suite (Stavoren: 2055.70 ± 1.0 Ma), and a granite from the Nebo/Lebowa granites (2054.23 ± 0.79 Ma). These ages indicate that mafic and felsic rocks of the Bushveld Complex are broadly coeval and support the proposal that some of the original magma volume in the intrusion was expelled to form the Upper Rooiberg Group lavas or Rashoop granophyres [3]. Below the Merensky Reef, there is a shift to older ages at ca. 2060 Ma. Results for two samples at different locations of footwall pyroxenite immediately below the UG-2 chromitite (Eastern Limb), ~380 m below the Merensky Reef, are 2060.5 ± 1.4 Ma and 2059.8 ± 1.2 Ma. It has long been recognized that initial Sr isotope ratios in both plagioclase and whole rocks increase sharply at the Merensky Reef over a few metres due to the emplacement of a compositionally distinctive magma batch [4]. The U-Pb geochronological results of this study indicate an age gap of perhaps as much as 5 million years between the uppermost Upper Critical Zone (UG-2 chromitite) and the Merensky Reef and overlying Main and Upper zones. The lowermost mafic-ultramafic rocks of the Bushveld Complex (Lower Zone and Critical Zone) appear to result from an earlier phase of magmatism at ca. 2060 Ma, coeval with the nearby 2060 Ma Phalaborwa carbonatite [5]. After a hiatus, now marked by the level of the Merensky Reef, the major volume of the Bushveld Complex was emplaced at ca. 2055 Ma.

[1] Scoates & Friedman (2008) *Econ. Geol.* **103**, 465-471. [2] Cawthorn & Walraven (1998) *J. Petrol.* **39**, 1669-1687. [3] VanTongeren *et al.* (2010) *J. Petrol.* **51**, 1891-1912. [4] Kruger & Marsh (1982) *Nature* **298**, 53-55. [5] Wu *et al.* (2011) *Lithos* **127**, 309-322.

Paleoproterozoic collapse in seawater sulfate and subsequent shallowing of the methane cycle in marine sediments

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The initial accumulation of atmospheric oxygen, referred to as the Great Oxidation Event or GOE, is fairly well-constrained to between 2,450 and 2,320 Ma. However, the magnitude and duration of that rise in oxygen is subject to debate. It is also not clear how the dynamic oxidation of the early Paleoproterozoic transitioned into the environmental stasis of the Boring Billion. In order to examine the history of Paleoproterozoic surface oxidation, we used a combination of pyrite multiple-sulfur (^{32}S, ^{33}S and ^{34}S) and organic carbon isotopes from marine black shales. We analyzed the (1) 2,320 Ma Rooihoogte and Timeball Hill Formations, from which the GOE is dated; (2) the 2,200 to 2,100 Ma Sengoma Argillite Formation, deposited during the peak of the Lomagundi carbon isotope excursion in an open-marine setting on the Kaapvaal craton; and (3) the Upper Zaonega Formation of the Ludikovian Series, Russian Karelia, deposited in a marine basin between 2,100 and 2,000 Ma, in the immediate aftermath of the Lomagundi carbon isotope excursion.

Pyrite S isotopes display large ^{34}S-^{32}S fractionations (>30‰) relative to seawater sulfate, indicating that a large marine sulfate reservoir (2-20 mM) developed as an immediate result of the GOE and persisted for nearly 250 Ma. In the aftermath of the Lomagundi carbon isotope excursion, pyrite sulfur isotope fractionations drop to <15‰, suggesting a rapid collapse of the marine sulfate reservoir to <200 μM. These low-sulfate conditions persisted for at least 600 Ma. Thus, it appears that the high oxidation state of the atmosphere-ocean system that developed as the immediate result of the GOE was largely lost by 2,000 Ma and did not return until the Ediacaran period. Accordingly, the Boring Billion is best described as a long-lived redox regime that was intermediate between those of the Archean and the early Paleoproterozoic, rather than between the early Paleoproterozoic and the Phanerozoic.

Organic carbon isotopes record a secular shift to more negative values at ca. 2,050 Ma, which is tightly coupled to the positive excursion in pyrite S isotopes. We interpret this carbon isotope excursion as an enhancement in the biological methane cycle in marine sediments as a result of the crash in seawater sulfate. As seawater sulfate concentrations dropped, methanogenesis operated closer to the sediment-water interface, setting up conditions suitable for subsequent methanotrophy and incorporation of ^{13}C-depleted biomass into the marine sedimentary organic carbon pool.