

U-Pb and Re-Os geochronology tracks stratigraphic condensation in the Sturtian snowball Earth aftermath

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ABSTRACT

The snowball Earth hypothesis predicts a strong hysteresis resulting in discrete multi-million-year glaciations followed by globally synchronous deglaciation. Here we present new U-Pb zircon and Re-Os sedimentary rock geochronology and Os isotope chemostratigraphy from post-Sturtian sequences in south China to test the synchronicity of deglaciation. High-precision chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) U-Pb zircon dates refine the minimum age of deglaciation to 660.98 ± 0.74 Ma, which is ~2 m.y. older than previously reported. We also provide a new maximum age constraint on the onset of the Marinoan glaciation of 657.17 ± 0.78 Ma. A global compilation of new Os isotope chemostratigraphy reveals a large and systematic trend to unradiogenic values over <1 m of stratigraphy. Together, these data indicate that the Mn-carbonates in south China are not cap carbonates that formed as a response to post-snowball alkalinity, but are authigenic carbonates that formed millions of years after deglaciation. Sturtian cap carbonates tend to be absent or more condensed than their younger Marinoan counterparts. We suggest that this reflects a combination of enhanced accommodation space in early Cryogenian under-filled rift basins, stronger hysteresis, larger ice volume, and/or higher CO₂ levels needed for deglaciation of the longer Sturtian glaciation. Further, our findings indicate that the apparent diachroneity of deglaciation can be explained readily as a consequence of stratigraphic condensation, itself due to the large post-Sturtian glacioeustatic transgressive sequence that outpaced shallow-water carbonate deposition.

INTRODUCTION

Neoproterozoic strata record evidence for two low-latitude glaciations. The distribution of these glacial deposits along with the association of iron formation and cap carbonates inspired the snowball Earth hypothesis (Hoffman et al., 1998; Kirschvink, 1992). The hypothesis predicts a strong hysteresis with ice-albedo runaway followed by the buildup of CO₂ past a critical threshold for deglaciation (Hoffman et al., 2017). The CO₂ threshold is strongly dependent on ice albedo, which may have varied between the two snowball events, but models predict discrete multi-million-year glaciations followed by globally synchronous deglaciation (Hoffman et al., 2017). Consequently, much debate around the nature of Neoproterozoic glaciations has focused on the number, duration, and synchronicity

of these events (Rooney et al., 2015; Spence et al., 2016; Zhou et al., 2019). These predictions are testable with precise geochronology.

The Sturtian and Marinoan glaciations have been bracketed in time with U-Pb chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) on zircon to between ca. 717 and 635 Ma (Condon et al., 2005; Macdonald et al., 2010; Calver et al., 2013; Prave et al., 2016; Zhou et al., 2019). Rooney et al. (2014) used the rhenium-osmium (Re-Os) sedimentary rock geochronometer to date the termination of the Sturtian glaciation and revealed that this snowball Earth glaciation lasted >56 m.y. At present, the geochronological database is consistent with two long-lived Cryogenian glaciations (Rooney et al., 2015; Zhou et al., 2019). However, Spence et al.

(2016) argued that the Re-Os geochronometer was untested because no locality had both U-Pb CA-ID-TIMS zircon and Re-Os dates on the same deposits, and that instead the Cryogenian glacial record could represent a Quaternary-like period of glacial-interglacial conditions (Allen and Etienne, 2008). Recent U-Pb CA-ID-TIMS zircon dates on the Sturtian deglaciation leave an apparent 4 m.y. gap between dates from within the uppermost glacial deposits in Australia of 663.03 ± 0.11 Ma (Cox et al., 2018) and from a purported cap carbonate in south China of 658.80 ± 0.50 Ma (Zhou et al., 2019). This could be interpreted to represent an exceptionally long orbitally forced deglaciation (Benn et al., 2015), diachroneity of deglaciation (Allen and Etienne, 2008), or extreme condensation of the post-glacial sequence in south China (Kennedy and Christie-Blick, 2011).

Here we present new age constraints using the Re-Os and U-Pb geochronometers on sedimentary rocks and air-fall tuff deposits, respectively, from strata that record the termination and post-deglaciation conditions of the Sturtian glacial event in south China. These data provide a temporal framework for the Sturtian deglaciation, and allow us to explore relationships between the different durations of the Sturtian and Marinoan glaciations and stratigraphic and geochemical differences in their deglacial sequences.

GEOLOGICAL SETTING

Cryogenian extension of the South China craton resulted in horst and graben structure and development of a southeast-facing continental margin (Yu et al., 2017; Bao et al., 2018). In basin settings, Sturtian diamictite of the Tiesi'ao Formation and equivalent units are separated

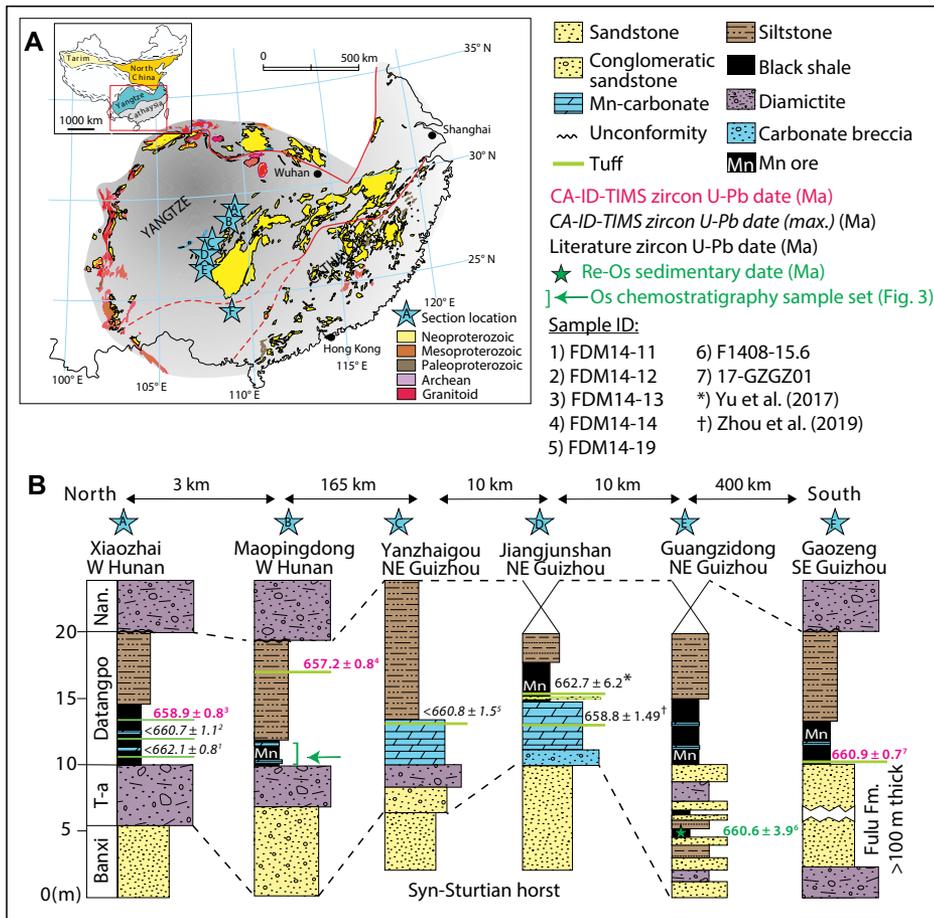


Figure 1. (A) Location map showing outcrop extent of Neoproterozoic strata on the South China craton. Inset shows main components of regional paleogeography. (B) Generalized stratigraphic columns of Neoproterozoic strata from Hunan and Guizhou Provinces, displaying U-Pb zircon chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) dates (green lines) and Re-Os isochron date (green star). Sample IDs are in superscript. T-a—Tiesi’ao Formation; Nan.—Nantuo Formation.

from Marinoan diamictite of the Nantuo Formation by thinly bedded shale and siltstone with minor carbonate of the Datangpo Formation (Fig. 1; Bao et al., 2018; Zhou et al., 2019). In locations, where the Sturtian diamictite is absent (e.g., the Jiangjunshan section), the Datangpo Formation unconformably overlies the Tonian Banxi Group (Fig. 1; Yu et al., 2017).

We collected samples for Re-Os and U-Pb geochronology and Os isotope chemostratigraphy from measured stratigraphic sections of the Datangpo Formation and underlying glacial deposits from the Yangtze block (Fig. 1; see the GSA Data Repository¹). In western Hunan, the Banxi Group is unconformably overlain by diamictite, sandstone, and conglomerate of the Tiesi’ao Formation. The overlying Datangpo Formation consists of <5 m of Mn-shale with

thin authigenic carbonate and tuff horizons, and <10 m of green laminated siltstone.

In Guizhou, conglomerate and dolomite of the basal Datangpo Formation overlie the Banxi Group (Fig. 1). In adjacent slope and basin sections, Mn-shale with authigenic carbonate rests above >2 km of diamictite of the Chang’an Formation and siliciclastic rocks of the Fulu Formation (Bao et al., 2018). At Guangzidong, ~10 m of interbedded sandstone, siltstone, shale, and stratified diamictite of the Tiesi’ao Formation with bed-penetrating dropstones grade into shale of the basal Datangpo (Fig. 1). We interpret these deposits as ice-rafted debris recording deglaciation, and sampled the interbedded shale for Re-Os geochronology.

RESULTS

Zircon was separated from nine mudstone horizons interpreted in the field as devitrified airfall ash deposits and dated with U-Pb CA-ID-TIMS (Figs. 1 and 2; Table DR1 in the Data Repository). The youngest concordant ²³⁸U–²⁰⁶Pb dates on zircon from samples

FDM14-11 and FDM14-12 provide maximum depositional ages (Fig. 2). Zircon from samples FDM14-13 and FDM14-14 yield concordant analyses of 658.97 ± 0.76 Ma (mean square of weighted deviates [MSWD] = 1.3) and 657.17 ± 0.78 Ma (MSWD = 1.3, n = 7), respectively, which we interpret as the eruptive and sedimentation age (Fig. 2). Two zircon grains from sample FDM14-19 are considered to be xenocrystic based on their morphology but yield ages <665 Ma. Zircon from sample 17GZGZ01 yielded seven concordant analyses with a weighted mean ²³⁸U–²⁰⁶Pb date of 660.98 ± 0.74 Ma (MSWD = 1.5, n = 7), which we interpret as the sedimentation age.

The Re-Os isotopic composition data from sample F1408-15.6 in the uppermost Tiesi’ao Formation yield a model 1 age of 660.6 ± 3.9 Ma (uncertainty includes the 0.35% ¹⁸⁷Re decay constant uncertainty [Smoliar et al., 1996]; n = 8, MSWD = 0.92, 2σ uncertainties, initial ¹⁸⁷Os/¹⁸⁸Os [Os]_i = 1.55 ± 0.05; Fig. 2; Fig. DR1; Table DR2). Initial Os isotope values for chemostratigraphy were generated from the black shale matrix of the Tiesi’ao diamictite and carbonaceous shale of the Datangpo Formation with an assumed deglaciation age of 660 Ma (Table DR3).

SYNCHRONOUS DEGLACIATION AND EXTREME CONDENSATION

On four paleocontinents, the termination of the Sturtian glaciation is marked by deposition of dark gray to black carbonaceous shales and limestones that sharply and conformably overlie glacial deposits. Here we provide a new Re-Os date of 660.6 ± 3.9 Ma from within the uppermost unit of a diamictite from south China (3 m below the overlying Datangpo Formation) that is within uncertainty of existing Re-Os ages from post-Sturtian sequences in Australia (Kendall et al., 2006; Cox et al., 2018), northwestern Canada (Rooney et al., 2014), and Mongolia (Rooney et al., 2015) (Fig. 2), suggesting that deglaciation was globally synchronous. Our new CA-ID-TIMS U-Pb dates from the Datangpo Formation of 660.98 ± 0.74 Ma, 658.97 ± 0.76 Ma, and 657.17 ± 0.78 Ma are also within uncertainty of the previously cited ages. These dates systematically young upsection and are oldest in sections away from paleo-highs (Fig. 1B). Incorporating our new CA-ID-TIMS U-Pb date from the lowermost Datangpo Formation, together with the onset age of 716.5 ± 0.2 Ma from northwestern Canada (Macdonald et al., 2010; Rooney et al., 2014), we augment the global data set and confirm that the duration of the Sturtian glaciation was 56 m.y. Critically, the new CA-ID-TIMS U-Pb dates for the final stages of the Sturtian glaciation agree with Re-Os dates, further demonstrating the validity of the Re-Os sedimentary rock chronometer (Fig. 2). Rather than a dia-

¹GSA Data Repository item 2020184, materials and methods, isochron figure, and data tables, is available online at <http://www.geosociety.org/datarepository/2020/>, or on request from editing@geosociety.org.

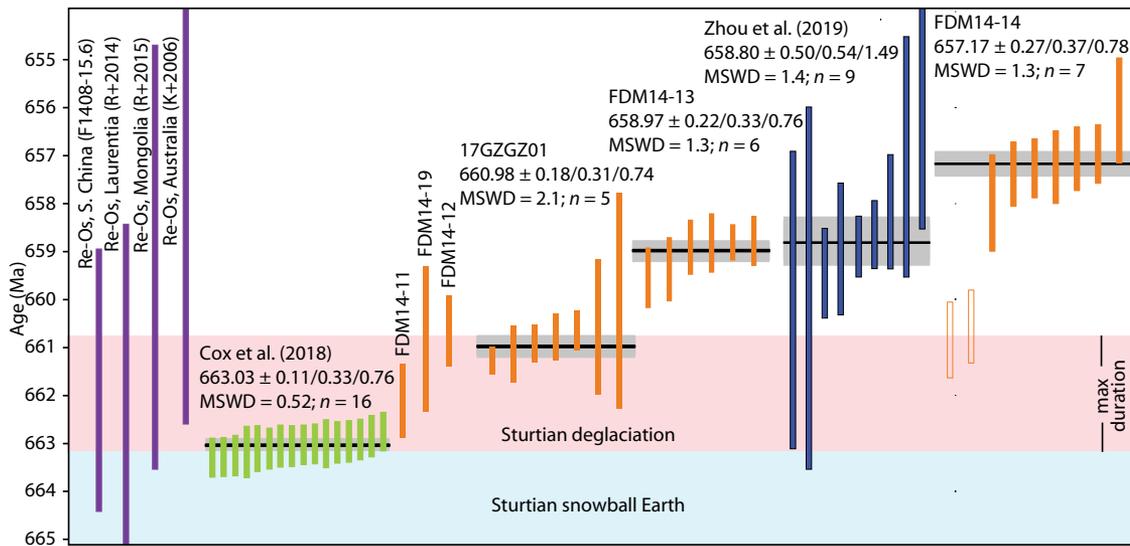


Figure 2. Compilation of zircon ^{238}U - ^{206}Pb and Re-Os dates. Vertical bars for ^{238}U - ^{206}Pb dates represent 2σ analytical uncertainty of individual zircon analyses, and unfilled bars are excluded in age calculations (Table DR1 [see footnote 1]). For samples FDM 14-11, FDM 14-12, and FDM 14-19, only the youngest concordant date of each sample is presented. Uncertainties in U-Pb dates are in the format X/Y/Z, where X is the analytical uncertainty, Y is the uncertainty incorporating the U-Pb tracer calibration error, and Z is the uncertainty including X and Y, as well as the uranium decay constant

uncertainty. Horizontal gray bands represent 2σ analytical uncertainties of weighted mean ^{238}U - ^{206}Pb dates. References for previous Re-Os ages: R+2014—Rooney et al. (2014); R+2015—Rooney et al. (2015); K+2006—Kendall et al. (2006). MSWD—mean square of weighted deviates.

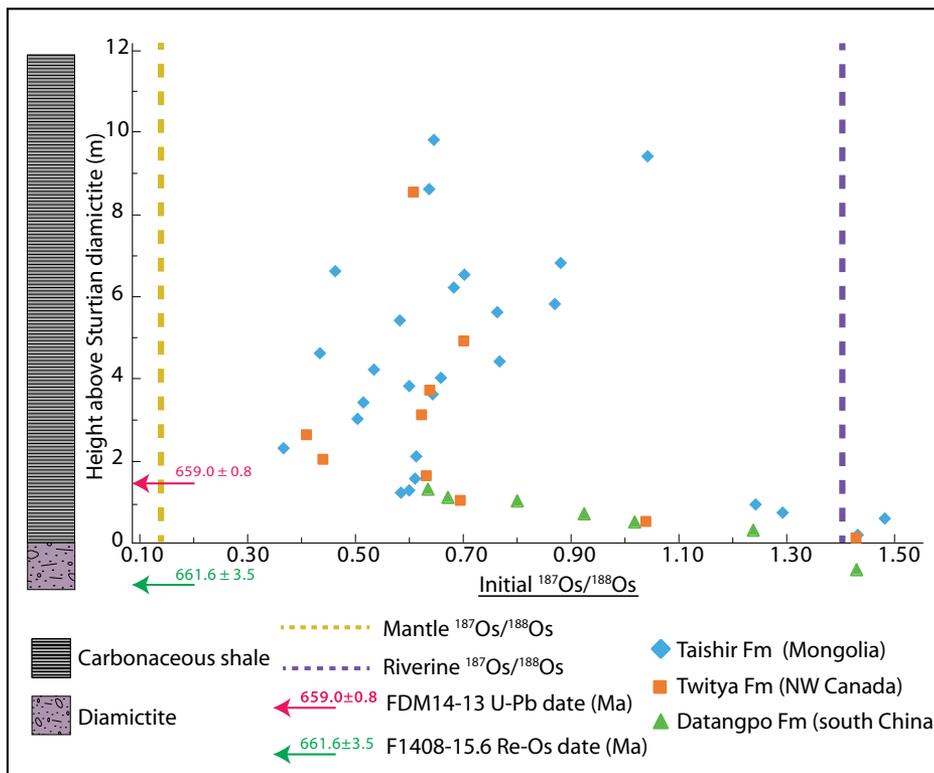


Figure 3. Composite post-Sturtian Os isotope chemostratigraphy. Initial south China data point is from sample F1408-15.6, within uppermost diamictite. Gold dashed line represents mantle Os flux (~ 0.13 ; Meisel et al., 2001), and purple dashed line is riverine Os flux (~ 1.5 ; Peucker-Ehrenbrink and Ravizza, 2000). Data for the Twitya and Taishir Formations are from Rooney et al. (2014, 2015).

chronous deglaciation, our new data are consistent with condensed deposition and onlap onto paleo-highs.

Previous constraints on the onset of the Marinoan glacial episode include a 639.3 ± 0.8 Ma CA-ID-TIMS U-Pb zircon date from within glacial deposits of Namibia

(Prave et al., 2016). The CA-ID-TIMS U-Pb zircon date of 657.17 ± 0.78 Ma presented here was collected above previously dated horizons from the Datangpo Formation, and thus supersedes existing U-Pb sensitive high-resolution microprobe (SHRIMP) data from south China (Zhang et al., 2008) for Mari-

noan glacial onset between 639.3 ± 0.8 Ma and 657.2 ± 0.8 Ma (Fig. 1).

POST-GLACIAL OSMIUM CHEMOSTRATIGRAPHY

The short residence time of Os in the ocean (<50 k.y.; Oxburgh, 2001) provides a complementary record to Sr isotope chemostratigraphy and post-glacial seawater chemistry in siliciclastic-dominated successions such as south China. During a snowball Earth, it is expected that the oceanic inventory of radiogenic isotopes would decrease in abundance and become unradiogenic with hydrothermal flux as the dominant source. Deglaciation under greenhouse conditions would result in a large flux of radiogenic riverine ions to the ocean.

At Maopingdong, the immediate post-glacial oceanic Os signal (<20 cm above diamictite) is highly radiogenic ($^{187}\text{Os}/^{188}\text{Os} > 1.4$), equivalent in composition to the average modern continental flux (Fig. 3; Table DR3; Peucker-Ehrenbrink and Ravizza, 2000). Values trend toward less-radiogenic values upsection, reaching ~ 0.7 at 1.3 m. Noteworthy is that the Os values from the uppermost diamictite and basal Datangpo Formation are comparable to those from post-Sturtian sections in Australia (Kendall et al., 2006), northwestern Canada (Rooney et al. 2014), and Mongolia (Rooney et al., 2015) (Fig. 3; Table DR3). We interpret these moderately radiogenic Os values as indicative of a well-mixed oceanic reservoir once the volumetrically larger unradiogenic snowball oceans began to dominate the signal. We suggest that the Datangpo data are not representative of cap carbonates *sensu* Hoffman (2011), but rather a condensed sequence that formed over millions of years during and after deglaciation (Fig. 3).

A TALE OF TWO SNOWBALLS

Our data confirm that the Sturtian glaciation was three to 18 times longer in duration than the Marinoan glaciation. Sturtian glacial deposits preserve iron formation, and are succeeded by an abrupt flooding surface with shale or limestone deposited below storm wave base (Giddings and Wallace, 2009). In contrast, Marinoan glacial deposits are succeeded by basal cap dolomites with shallow-water facies culminating in sedimentary barite and aragonite fans (Hoffman, 2011).

Many Sturtian margins were likely over-deepened and starved due to Tonian and early Cryogenian rifting and low sediment accumulation rates over the ~56 m.y. Sturtian glaciation. During the Cryogenian nonglacial interlude, these basins were likely filled, as reflected by thick successions in Namibia (Halverson et al., 2002), Australia (Giddings and Wallace, 2009), and northwestern Canada (Rooney et al., 2014), which culminate with shallow-water deposits. By the Marinoan, many of the Rodinia rifted margins had entered a thermal subsidence stage, so tectonic accommodation was reduced relative to the Sturtian. Combined with a shorter duration with low syn-glacial sedimentation rates (Partin and Sadler, 2016), less tectonic accommodation during the Marinoan glaciation should have resulted in a higher base level and shallower-water deposits in the Marinoan aftermath relative to the Sturtian.

Previous work suggested strong orbital forcing and ice volume reduction during the latest stages of the Marinoan glaciation (Benn et al., 2015). Rather than an abrupt transition from icehouse to greenhouse, Kennedy and Christie-Blick (2011) explained the juxtaposition of cap carbonates with glacial strata as the result of extreme condensation during cyclic transgressions. However, no such cycles have been reported in Sturtian glacial or post-glacial deposits, so we find no evidence of ice volume reduction or a weak hysteresis at the end of the Sturtian glaciation.

Condensation, reflected by a more rapid transgressive systems tract relative to carbonate deposition, could be a product of the relative greenhouse forcing between the Marinoan and Sturtian glaciations. The threshold of pCO_2 needed for deglaciation is controlled by the ice albedo (Pierrehumbert et al., 2011). With as much as 21 m.y. between the end of the Sturtian and the beginning of the Marinoan glaciation, at typical plate tectonic speeds of 2–8 cm/yr, a continent could have drifted in or out of the tropics over this interval, and dramatically changed dust production and albedo. If the planet was also more weatherable due to the mantling of the surface by large igneous provinces (Macdonald et al., 2010; Cox et al., 2016) or additional arc terranes or rift-related basalts in the tropics (Gernon et al., 2016; Park et al.,

2019), or if there was an increased sink due to higher relative seafloor weathering during the Sturtian (Le Hir et al., 2008), then a higher pCO_2 level would have been necessary to initiate deglaciation, leading to the longer duration of the Sturtian. Future geochemical investigations on pre- and post-glacial sedimentary archives will focus on evaluating the role(s) played by these geological forcings that led to the disparity in glacial durations.

CONCLUSIONS

We provide a new constraint on the minimum age of Sturtian deglaciation at 660.98 ± 0.74 Ma, and a maximum age of Marinoan onset at 657.17 ± 0.78 Ma. The Re-Os isochron age of 660.6 ± 3.9 Ma is compatible with these U-Pb CA-ID-TIMS zircon ages, again confirming the utility of the Re-Os geochronometer. The apparent diachroneity of deglaciation is interpreted as the product of condensation in post-glacial stratigraphy rather than actual diachronous deglaciation. We suggest that a longer duration, stronger hysteresis, and greater tectonic accommodation during the Sturtian relative to the Marinoan glaciation resulted in the stratigraphic and sedimentological differences between the two post-glacial sequences. A composite Os isotope profile from globally distributed post-glacial sequences reveals a secular change to the global ocean Os composition. This chemostratigraphic profile highlights a trend from highly radiogenic Os values at the onset of deglaciation to unradiogenic, mantle-like values indicative of “snowball deepwater” before a return to moderately radiogenic values further upsection.

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