Stable Isotope Evidence for Hydro-Chemical Processes in Groundwater of the Oyu Tolgoi Copper Mine, Mongolia

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Abstract

Groundwater protection in mining regions requires early identification of contamination sources, though this remains challenging in complex hydrogeological settings. This study integrates major ion chemistry with stable isotopes of water ($\delta^{18}O$) and sulfate ($\delta^{34}S$, $\delta^{18}O$) to distinguish natural processes from mining influences in the Oyu Tolgoi region. Water isotopes indicate meteoric origin with strong evaporation, while sulfate isotopes reflect sulfide oxidation under open conditions. Large fractionation occurs in natural systems, whereas tailings seepage shows enriched sulfate $\delta^{18}O$ and high sulfate concentrations, indicating enhanced oxidation. Salinity is mainly driven by evaporation, while sulfate derives from dissolution and oxidation, supporting improved groundwater monitoring and sustainable management.

Keywords: Oyu Tolgoi, sulfur and water isotope signatures, sulfur oxidation, evaporation

Introduction

Early identification of groundwater contamination sources is critical in mining regions due to reliable source attribution is often complicated by the overlap of natural hydro-chemical processes and mining related influences. In complex hydrogeological settings, major ion chemistry alone is insufficient to distinguish baseline groundwater conditions from potential mining impacts. In such cases, integrating isotopic tracers with geochemical data provides an effective approach for resolving hydro-chemical processes and improving discrimination between natural background signals and anthropogenic inputs. At the Oyu Tolgoi (OT) copper mine, elevated total dissolved solids (TDS) were detected in a shallow monitoring bore screened within an alluvial aquifer downgradient of mining infrastructure. To investigate the potential causes of this salinity increase, Puntsag *et al.* (2025) applied a multivariate approach combining stable isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{34}S$), radiogenic isotopes ($^{87}Sr/^{86}Sr$), and major and trace element geochemistry. Their results indicated that evaporative enrichment and mineral dissolution are the dominant controls on groundwater salinity, with no clear evidence of direct mining related inputs. However, the origin and geochemical evolution of dissolved sulfate and its potential links to mining processes remain insufficiently constrained. The sulfur and oxygen isotopic composition of dissolved sulfate ($\delta^{34}S$ and $\delta^{18}O$) is widely applied to distinguish sulfate sources and oxidation processes in mining environments (Krouse and Mayer 2000; Dold and Spangenberg 2005). Sulfate derived from sulfide oxidation typically reflects the $\delta^{34}S$ signature of the parent sulfide minerals, whereas sulfate produced by evaporite dissolution generally exhibits more positive $\delta^{34}S$ values. In contrast, $\delta^{18}O$ values provide insight into oxidation pathways and groundwater mixing processes, making the combined $\delta^{34}S$–$\delta^{18}O$ isotope system an effective tool for evaluating sulfate origin and geochemical evolution in mine affected aquifer systems (Kim *et al.* 2019). In OT, the flotation circuit mineralogy is dominated by sulfide minerals, primarily chalcopyrite, with subordinate amounts of bornite, chalcocite, pyrite, and enargite.

These sulfide minerals typically exhibit $\delta^{34}S$ values ranging from negative to near zero. In contrast, associated sulfate minerals such as gypsum, anhydrite, and alunite from the Central deposit are characterized by strongly positive $\delta^{34}S$ values, reflecting distinct reduced sulfide and oxidized sulfate sulfur reservoirs (Khashgerel *et al.* 2006). Similar isotopic contrasts observed in other mine tailings and groundwater systems demonstrate the utility of $\delta^{34}S$ for discriminating sulfate derived from sulfide oxidation versus evaporite dissolution, while $\delta^{18}O$ provides complementary information on oxidation mechanisms and secondary sulfate formation processes (Dold and Spangenberg 2005; Kim *et al.* 2019; Natali *et al.* 2025). The objective of this study is to characterize the sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) isotopic composition of dissolved sulfate (SO_4^{2-}) in groundwater associated with copper ore processing operations at the OT mine. Isotopic analyses were conducted on precipitation, deep regional groundwater, process water components (including thickener overflow and barge water), tailings storage facility (TSF) seepage waters, and groundwater samples from multiple hydrogeological units. All samples were collected contemporaneously across the site

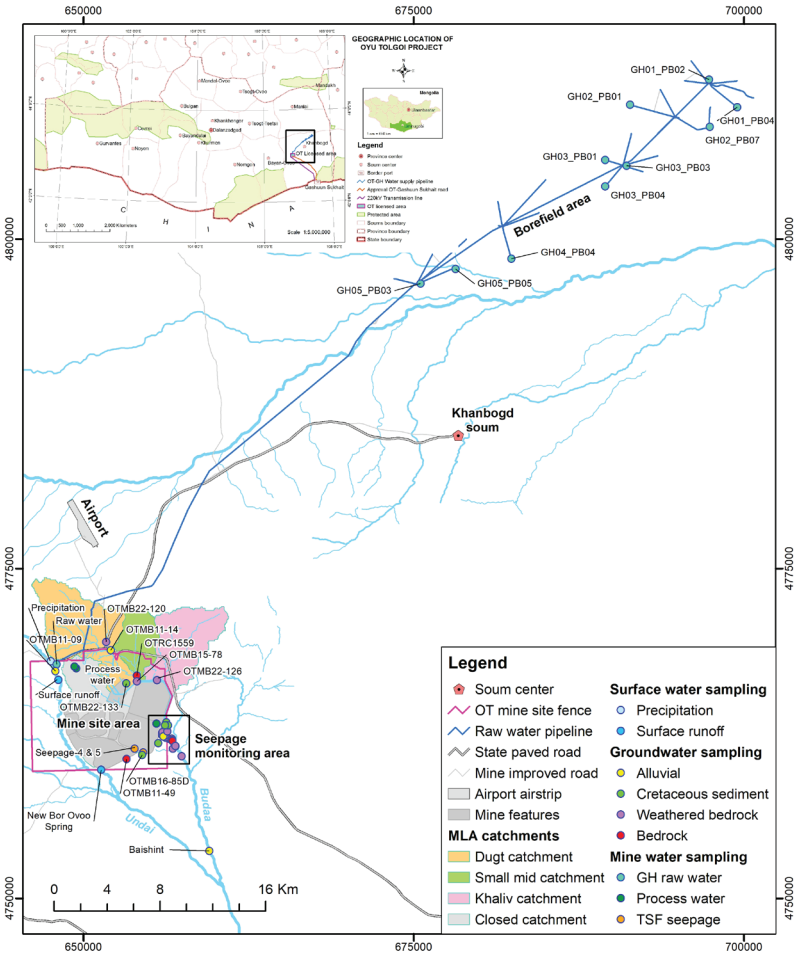

Figure 1 *OT mine site, sampling locations (from Puntsag* et al. *2025): wet precipitation, source water, process water, thickener overflow, the barge pond, seepage collection ponds, and groundwater (alluvial, Cretaceous sediments, weathered bedrock, and bedrock).*

to ensure temporal consistency. Evaluation of $\delta^{34}S$ and $\delta^{18}O$ isotopic data provides new insights into sulfate sources, mixing relationships, and transformation processes influencing groundwater chemistry at OT, thereby supporting improved assessment of mining related impacts and long-term groundwater management.

Method

This study was conducted at the OT copper mine in South Gobi, Mongolia (43000' N, 106050' E). In 2024, a two day focused sampling campaign collected more than 75 water samples along the mine water system, extending from the Gunii Khooloi borefield through the processing circuit to the downstream monitoring network east of the TSF (Fig. 1).

The study area has no notable groundwater withdrawal impacts causing sulfide oxidation or acid mine drainage, and mining-related sulfate is primarily introduced during ore processing rather than through hydrogeological disturbance. Water samples were collected in 15 mL glass vials (for hydrogen and oxygen isotopes) and 250 mL HDPE bottles (for sulfur isotope), including blanks and random duplicates with appropriate storage conditions maintained during shipment, as directed under analytical services provided by the West Australian Biogeochemistry Centre and the ICP-MS laboratory at the Centre for Microscopy, Characterization and Analysis. Hydrogen and oxygen isotope ratios were measured using a Picarro L2130 i cavity ring down spectroscopy (CRDS) analyses. All values were normalized to the VSMOW scale using three laboratory reference waters calibrated against IAEA standards (VSMOW2, SLAP2, and GISP). Sulfur isotope compositions ($\delta^{34}S$) were reported relative to the Vienna–Canyon Diablo Troilite (V CDT) scale. Analyses were undertaken on a Sercon 20 22 isotope ratio mass spectrometer coupled with an elemental analyzer. Isotopic measurements were performed using isotope ratio mass spectrometry with analytical precision better than ±0.2‰ for $\delta^{18}O$ and ±0.3‰ for $\delta^{34}S$.

The ANOVA-Analysis of Variance and other statistical analyses for the data has been performed using JMP Pro 16.2 (Hummel *et al.*, 2021).

Result and discussion

In the initial stage of this study, $\delta^{34}S$ isotopic compositions showed strong negative correlations with Ca, K, Sb, Cd, Mo, Rb, and Sr, ranging from −0.72 to −0.95. These relationships indicate that sulfur isotope variations are tightly coupled to the geochemical behavior of redox sensitive chalcophile elements (Goldschmidt, 1937; Rollinson, 2014) as well as to the mobilization and transport of alkali and alkaline earth elements. Together, these relationships underscore the dominant role of sulfur driven processes in shaping broader geochemical system responses.

As shown in Fig. 2, mean $\delta^{18}O$ of water (‰, VSMOW) differs significantly among water types ($F(8,62) = 11.08$, $p < 0.0001$), with water type explaining approximately 59% of the total variance ($R^2 = 0.59$). This result demonstrates strong isotopic differentiation between natural waters, deep groundwater, and mining related waters. Similarly, $\delta^{18}O$ of sulfate (‰ SO_4) shows significant variation among groups ($F(8,63) = 10.38$, $p < 0.0001$, $R^2 = 0.57$), indicating that sulfate oxygen isotopes are sensitive to differences in sulfur source and formation processes across water types.

$\delta^{34}S$ (‰, VCDT) also varies significantly among water types ($F(8,63) = 9.99$, $p < 0.0001$), with type accounting for 56% of the observed variance ($R^2 = 0.56$). This statistically significant separation reflects contrasts between geogenic sulfur sources and mining influenced sulfur derived from sulfide oxidation. In contrast, sulfate concentrations (SO_4^{2-}, mg/L) do not differ significantly among water types ($F(7,60) = 1.48$, $p = 0.19$), and the proportion of variance explained by type is low ($R^2 = 0.15$). This indicates substantial within group variability and highlights the limited discriminatory power of concentration data alone. Overall, the ANOVA results demonstrate that isotopic parameters provide robust and statistically significant differentiation among water types, whereas sulfate concentrations are comparatively insensitive to source

and process variability. As shown in Fig.3, $\delta^{18}O_{water}$ values are consistently negative (approximately −6 to −11‰), reflecting meteoric water signatures, whereas $\delta^{18}O_{sulfat}$e values are positive (approximately +2 to +5‰). The vertical separation between these two bars for each group corresponds to $\Delta\delta^{18}O_{sulfate}$-$\delta^{18}O_{water}$ which is uniformly large across all sample types (approximately 11–13‰). If sulfate were derived primarily from gypsum ($CaSO_4 \times 2H_2O$) dissolution, $\delta^{18}O_{sulfate}$ would largely reflect the fixed isotopic composition of the mineral and tend toward isotopic equilibrium with ambient water over time (Taylor *et al.* 1984; Dogramaci *et al.* 2001), resulting in smaller or more variable $\Delta\delta^{18}O_{sulfate}$-$\delta^{18}O_{water}$ values, typically less than 5‰.

The coupled $\Delta\delta^{18}O_{sulfate}$-$\delta^{18}O_{water}$ relationships provide definitive evidence for sulfate generation dominated by oxidative sulfide oxidation rather than gypsum dissolution. Across all water types, large and consistent $\Delta\delta^{18}O_{sulfate}$-$\delta^{18}O_{water}$ (11–13‰) persist, indicating incorporation of atmospheric O_2 into sulfate during oxidation and sustained isotopic disequilibrium with ambient water (Taylor *et al.* 1984; Dogramaci *et al.* 2001). Gypsum dissolution is ruled out because it would yield sulfate with relatively invariant $\delta^{18}O$, smaller sulfate water difference, diagnostic Ca–SO_4 stoichiometry, and minimal linkage to redox sensitive elements (Seal, 2006; Blowes *et al.* 2014). As shown in Fig. 4, background waters (deep aquifer, bedrock, weathered bedrock, and

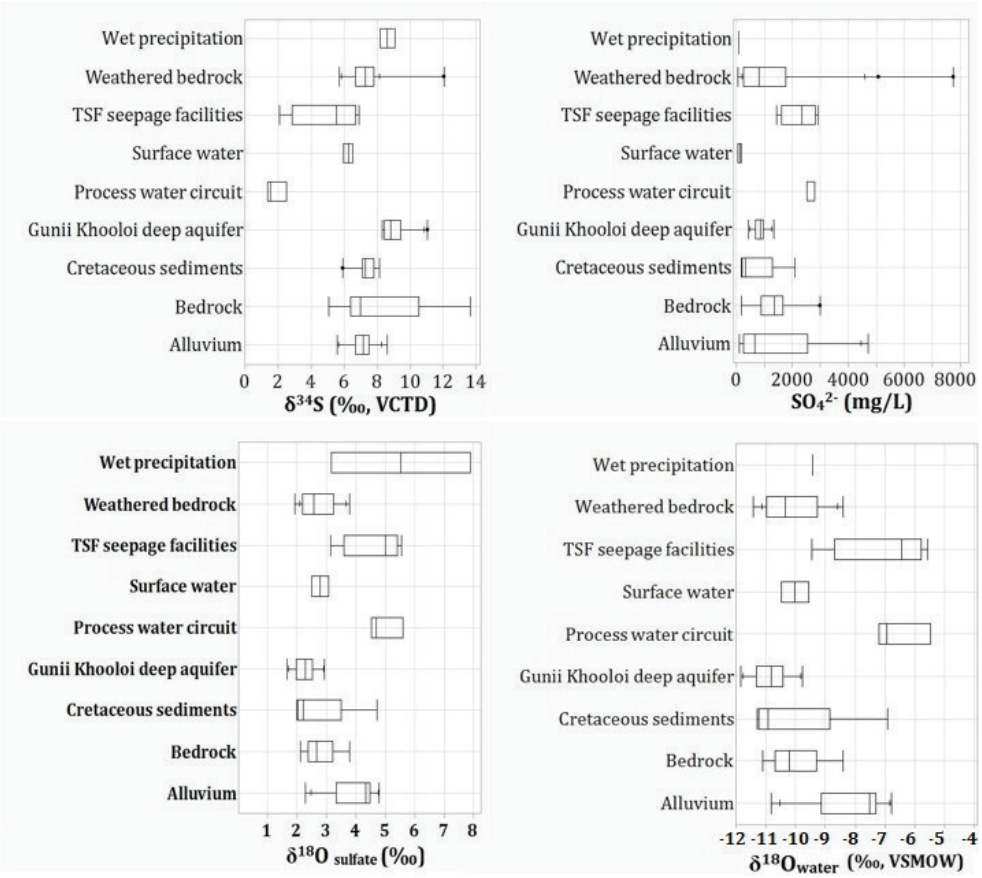

Figure 2 Quantile box plots showing statistical distribution of $\delta^{18}O$water (‰), $\delta^{18}O$sulfate (‰), $\delta^{34}S$ (‰, VCTD), and SO_4^{2-} (mg/L) across water sources and hydrogeological units; boxes indicate the 25th–75th percentiles, the central line indicates the median, and whiskers indicate the data spread.

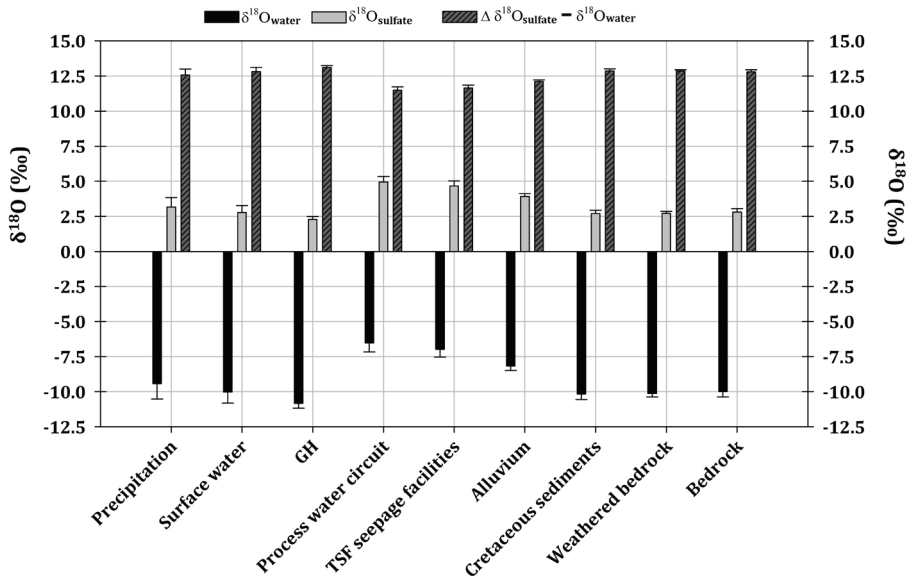

Figure 3 *Mean $\delta^{18}O$ of water and $\delta^{18}O$ of sulfate, and their difference ($\Delta\delta^{18}O_{sulfate}$-$\delta^{18}O_{water}$), across water sources, process circuit water and groundwater monitoring bores of different hydrogeological units.*

surface water) cluster within a relatively narrow $\delta^{34}S$ range (6–9‰) and generally at lower to moderate sulfate concentrations. These samples fall largely within the native $\delta^{34}S$ envelope, indicating minimal isotopic perturbation. In contrast, TSF seepage and process water samples plot at higher sulfate concentrations and show systematically lower $\delta^{34}S$ values, extending well below the lower limit of the native range. The strong negative trend between $\delta^{34}S$ and sulfate concentration ($\delta^{34}S = 11.2 - 0.003 \times SO_4^{2-}$, R^2adj =-0.74, p = 0.009) demonstrates that increasing sulfate is associated with progressive sulfur isotope depletion. If sulfate were derived primarily from gypsum dissolution, $\delta^{34}S$ values would remain relatively constant and constrained by the evaporite source, regardless of sulfate concentration. Instead, the observed trend reflects active sulfur redox cycling, with increasing sulfate production accompanied by isotopic fractionation during sulfide oxidation. The clear separation between background waters and process affected waters therefore indicates that mining related sulfur oxidation is the dominant control on sulfate generation in impacted zones, while natural waters retain their native sulfur isotopic signature. Most samples cluster within a $\delta^{34}S$ range of approximately 6–10‰ and $\delta^{18}O_{sulfate}$ values of 2–4‰, corresponding to background waters such as bedrock, weathered bedrock, surface water, and the Gunii Khooloi deep aquifer. In contrast, samples from the process water circuit and TSF seepage plot toward lower $\delta^{34}S$ values and higher $\delta^{18}O_{sulfate}$ values. These impacted waters define a clear inverse trend, captured by the regression $\delta^{18}O_{sulfate} = 5.66 - 0.34 \times \delta^{34}S$ (R^2adj = 0.62, p = 0.0073, n = 9), indicating that progressive sulfur isotope depletion is accompanied by enrichment in sulfate oxygen isotopes.

The observed negative relationship between $\delta^{34}S$ and $\delta^{18}O_{sulfate}$ is characteristic of oxidative sulfide weathering, where sulfate is newly generated rather than inherited from pre existing sulfate minerals. During sulfide oxidation, sulfur retains the isotopic signature of the sulfide source (often isotopically light), while sulfate oxygen incorporates a substantial proportion of oxygen from atmospheric O_2, leading to enrichment in $\delta^{18}O_{sulfat}$e. This coupled isotopic behavior cannot be explained by gypsum dissolution, which would produce relatively constant $\delta^{18}O_{sulfate}$ values largely independent of $\delta^{34}S$ and ambient water. Instead, the systematic

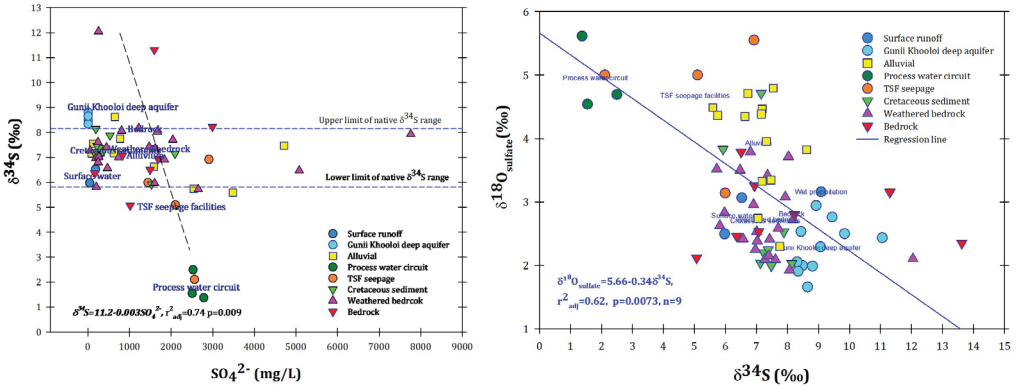

Figure 4 Relationships among variables (n = 72) for water sources, process water, and groundwater across hydrogeological units; dashed horizontal lines indicate background $\delta^{34}S$ limits, and a dashed regression line shows the $\delta^{34}S$–sulfate relationship for process-affected waters.

covariation documented in the figure demonstrates active sulfur redox cycling, with mining affected waters recording the strongest expression of oxidative sulfur processes, while background waters retain more uniform, native isotopic signatures.

The conceptual model (Fig.5) summarizes the evolution of sulfur isotopes ($\delta^{34}S$) from background waters through mining affected systems and into downgradient environment. Wet precipitation and the Gunii Khooloi deep aquifer define a narrow native $\delta^{34}S$ range (8–9‰), representing background geogenic sulfur.

In contrast, process water exhibits markedly depleted $\delta^{34}S$ values (2‰), reflecting sulfate generation dominated by oxidative sulfide weathering. As impacted waters migrate through the TSF seepage facilities, $\delta^{34}S$ values shift toward intermediate compositions (5–6‰), indicating secondary modification through evaporation, concentration, and mixing with background sulfate. Downgradient aquifers show further convergence toward native $\delta^{34}S$ values, consistent with progressive attenuation and hydrologic mixing. Overall, the isotopic evolution highlights sulfur driven redox processes as the primary control on sulfate generation in mining affected waters, with subsequent partial re equilibration during subsurface transport.

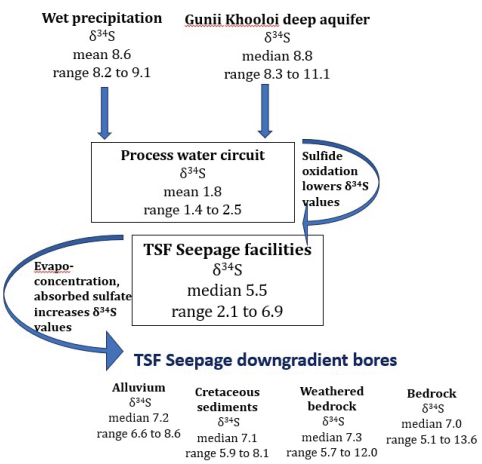

Figure 5 Summary of inputs, outputs and processes that affect $\delta^{34}S$ values. Units are ‰. Further information is provided in the text.

Conclusion

This study demonstrates that coupled sulfur and oxygen isotope systematics provide a robust framework for identifying sulfate sources and mining influences in the OT hydrogeological system. For the first time, precipitation, process water, TSF seepage, surface water, and groundwater were evaluated together using integrated $\delta^{34}S$, $\delta^{18}O_{sulfate}$, and $\delta^{18}O_{water}$ tracers. One way ANOVA shows

that isotopic compositions differ significantly among water types ($p < 0.0001$), whereas sulfate concentrations alone show limited separation. Large and consistent sulfate–water isotope offsets ($\Delta^{18}O$ =11–14‰) and negative $\delta^{34}S$–$\delta^{18}O$ relationships indicate sulfate generation dominated by open system oxidative sulfide weathering, ruling out gypsum dissolution. Mining affected waters show distinct sulfur isotopic signatures and trace element associations, confirming sulfur isotopes as effective tracers of anthropogenic influence. Overall, OT remains far from acid mine drainage conditions, with regional background processes dominating.

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