



High-sensitivity measurement of diverse vascular plant-derived biomarkers in high-altitude ice cores

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[1] Semi-volatile organic compounds derived from burned and fresh vascular plant sources and preserved in high-altitude ice fields were detected and identified through use of recently developed analytical tools. Specifically, stir bar sorptive extraction and thermal desorption coupled with gas chromatography/time-of-flight mass spectrometry allowed measurement of multiple biomarkers in small sample volumes (≤ 30 ml). Among other compounds of interest, several diterpenoids, which suggest inputs from conifers and conifer burning, were identified in post-industrial era and older Holocene ice from the Sajama site in the Bolivian Andes, but not in a glacial period sample, consistent with aridity changes. Differences in biomarker assemblages between sites support the use of these compounds as regionally constrained recorders of vegetation and climate change. This study represents the first application of these analytical techniques to ice core research and the first indication that records of vegetation fires may be reconstructed from diterpenoids in ice. **Citation:** Makou, M. C., L. G. Thompson, D. B. Montluçon, and T. I. Eglinton (2009), High-sensitivity measurement of diverse vascular plant-derived biomarkers in high-altitude ice cores, *Geophys. Res. Lett.*, 36, L13501, doi:10.1029/2009GL037643.

1. Introduction

[2] Molecular markers or biomarkers (organic compounds attributable to specific precursor organisms) derived from vascular plants have been identified in sediments from many depositional settings and have been used to reconstruct past changes in climate parameters such as vegetation type, atmospheric circulation, and aridity [e.g., *Gagosian and Peltzer*, 1986; *Kawamura et al.*, 1996; *Makou et al.*, 2007]. Rapid aeolian transport and deposition [*Conte and Weber*, 2002], as well as the excellent preservation potential of vascular plant biomarkers support their use as paleoclimate indicators. Leaf wax compounds and plant combustion byproducts such as polycyclic aromatic hydrocarbons (PAHs), vanillic acid, and levoglucosan, have been shown to occur in high-altitude and polar ice [*Kawamura et al.*, 1994, 1996; *Currie et al.*, 1998; *Xie et al.*, 2000; *McConnell et al.*, 2007; *Gambaro et al.*, 2008], but are generally an

underutilized resource in this medium due to their low ambient concentrations, which typically necessitate processing of kilogram quantities of ice for analysis or are limitation to a single molecular species. Here we explore the organic geochemical information encoded in ice cores using analytical techniques that promote monitoring of multiple vascular plant-derived compounds while limiting sample sizes.

[3] High-altitude tropical ice cores have yielded invaluable insights into low-latitude climate variability since the last glacial period [e.g., *Thompson et al.*, 1997, 1998]. Observations of vascular plant fragments and pollen in these cores demonstrate effective aeolian delivery of vegetation-derived organic matter to remote ice fields from the last glacial period to the present [*Thompson et al.*, 1998; *Liu et al.*, 2005]. We examined post- and pre-industrial era samples from several high-altitude ice cores in order to establish the utility of our approach and extract additional lines of climate information from these valuable archives. We analyzed post-industrial ice from the Huascarán and Sajama sites in the Andes, the Dasuopu and Puruogangri cores from the Tibetan Plateau, and Mt. Kilimanjaro in Africa (Figure S1 and Table S1 of the auxiliary material).¹ The pre-industrial investigation included two Holocene samples (approximate ages 2 and 5 ka) and one glacial period sample from Sajama, as well as two Holocene samples (approximate ages 2 and 6 ka) from the Puruogangri site. This array of sample locations and ages provided the opportunity to compare the biomarker content of ice collected from regions with differing climates and vegetation.

[4] Several previous studies have confirmed the presence of biomarkers in snow and ice deposited both recently and prior to the industrial era [*Grannas et al.*, 2006]. Some of these investigations have produced historical records [*Kawamura et al.*, 1994, 1996; *McConnell et al.*, 2007], although large sample volumes were typically required for these analyses or limited chemical species were monitored. For example, *Kawamura et al.* [1994, 1996] measured total alkanolic acid (fatty acid) and non-alkylated PAH concentrations of up to 105 ng/g (C_{12} – C_{32}) and 230 pg/g, respectively, in Greenland ice samples spanning the last 400 years, using sample volumes of about 350 ml. PAHs have been identified in kilogram quantities of ice and snow [*Peters et al.*, 1995; *Masclat et al.*, 2000], and *Currie et al.* [1998] quantified individual PAHs in as little as 120 g of contemporary Greenland snow. The methods we test and employ here provide a means to identify and quantify numerous compounds while reducing sample volumes, with

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the goal of facilitating development of future multi-molecular proxy records from ice cores.

2. Methods

[5] We employed recently developed analytical technology to characterize the semi-volatile lipid content of ice core samples equivalent to 30 ml or less. Specifically, stir bar sorptive extraction (SBSE) and thermal desorption (TD) were used to extract and concentrate organic matter from the melted ice and then transfer it to a gas chromatograph (GC) coupled to a time-of-flight mass spectrometer (TOF-MS), which provided the means of compound identification and quantitation. To perform SBSE, a glass-encapsulated magnetic stir bar coated with a polydimethylsiloxane (PDMS) phase is spun in an aqueous sample, during which time analytes are partitioned into the phase through absorption [Baltussen *et al.*, 1999]. SBSE has been used successfully in this manner to analyze such compounds as fatty acids, amines, and PAHs [Popp *et al.*, 2001; Pfannkoch *et al.*, 2003], with <0.1 ng/L detection limits for some pollutants [Baltussen *et al.*, 1999]. TD, which involves heating the stir bars under a He flow, provides a means of quantitatively transferring the sorbed organic matter from the stir bar to the GC inlet for subsequent separation and detection via TOF-MS. The high spectral acquisition rates inherent to TOF-MS allow use of fast-GC techniques that increase chromatographic peak amplitude, and thus the signal-to-noise ratio, aiding in quantification of low abundance molecular species. Details pertaining to sample preparation, analytical parameters, and compound detection and quantification are provided as auxiliary material.

3. Results and Discussion

[6] Many of the melted ice samples contained visible grains, which were often dark in color in the post-industrial, or “modern”, samples. Granular recalcitrant organic matter, woody plant fragments, and organic carbon-coated mineral grains were identified in the post-industrial Sajama sample by light microscopy. The presence of mineral grains in ice represents a problem for successful extraction of organic matter via SBSE because some analytes could be tightly bound to solids, potentially excluding them from our analytical window. A radiocarbon analysis (conducted at NOSAMS) was performed on particulate organic carbon recovered by filtration from the Huascarán, Sajama, and Kilimanjaro post-industrial ice core samples (~300 ml each) in order to assess contributions of aged and/or petrogenic material. Only these samples were analyzed due to required carbon abundances for accelerator mass spectrometry ^{14}C measurements. The ^{14}C ages determined for these samples were 2,200 (± 240) years for Huascarán, 7,140 (± 210) for Sajama, and 880 (± 150) for Kilimanjaro. These results demonstrate that a portion of the particulate organic matter delivered to these ice fields consists of aged material; whether this older fraction resulted from fossil fuel burning or weathering of soils and sediments remains uncertain. The composition of particulate organic matter appears to be highly variable between sites, even among those from within the Andes. However, aged organic matter preserved through close association with mineral surfaces is

likely not recoverable via SBSE and thus would not impact records generated using our methods.

[7] The diterpenoid compounds dehydroabietane, dehydroabietic aldehyde (dehydroabietal), and sugiol (12-hydroxy-13-isopropyl-podocarpa-8,11,13-trien-7-one), all of which (Figure S2) are chemical variants of the dehydroabietic acid skeleton and are suggestive of biomass burning and coniferous vegetation sources, were identified only in Sajama ice core samples and were not detected in any blanks (Figure 1 and Table S2). Dehydroabietane and dehydroabietic aldehyde have been observed in smoke particulates from combusted conifers and emissions from softwoods burned in wood stoves [Oros and Simoneit, 2001a; Fine *et al.*, 2004]. Dehydroabietane is a naturally occurring and abundant compound in conifers but can also be produced through abietic acid alteration [Otto and Simoneit, 2001], and dehydroabietic aldehyde is a conifer resin oxidation product [Oros and Simoneit, 2001a]. Sugiol, which has a similar chemical structure to dehydroabietane (Figure S2), is a natural component of many types of coniferous vegetation, except for members of the Pinaceae family [Otto and Simoneit, 2001]. It has been observed in seed cone extracts from a present-day cypress and fossil seed cone extracts from Eocene and Miocene plants [Otto *et al.*, 2002]. The presence of these biomarkers implies that organic carbon inputs to the Sajama ice cap from vegetation fires include both fresh and thermally altered material. Also, the presence of sugiol, which is a polar and labile compound, suggests that a wide range of compounds liberated from vascular plants through ablation or combustion could be preserved in high-altitude glaciers and recovered using SBSE and TD. The diterpenoid biomarkers identified in this study indicate that conifer combustion and subsequent aeolian smoke delivery is a source of trace organic material to the Sajama ice cap. Minor amounts of *Podocarpus* pollen have been observed in Sajama ice from the last 400 years, and may have been derived from vegetation on the lower eastern Andean slopes [Liu *et al.*, 2005], confirming a possible source for the conifer-specific burning markers that characterize Sajama ice.

[8] The benzofuran tremetone (2,3-dihydro-2-isopropenyl-5-benzofuranyl methyl ketone) (Figure S2), a putative vascular plant marker, was identified in all of the modern ice core samples. It has been identified in extracts from rayless goldenrod [Zalkow *et al.*, 1979] and an Argentinean plant of the Asteraceae family [Uriburu *et al.*, 2007], and has also been found in Brazilian propolis, which is a constituent of honeybee hives originating from local vegetation [Banskota *et al.*, 1998]. This compound was observed in samples from all five sites (Figure 1), but occurred in the greatest abundances in the Sajama samples and was not detected in any blanks (Table S2). The average concentration of tremetone in the modern Sajama samples was 99 pg/ml, while samples from the other cores exhibited concentrations ranging between 2 and 7 pg/ml. Abundant amounts of Asteraceae pollen have been observed in Sajama ice and are attributed to high-altitude plant communities [Liu *et al.*, 2005], suggesting that a local vegetation source could account for the enhanced tremetone inputs observed in this core. The presence of tremetone is consistent with that of other natural vascular plant products released during the burning process [Oros and Simoneit, 2001a]. Because this

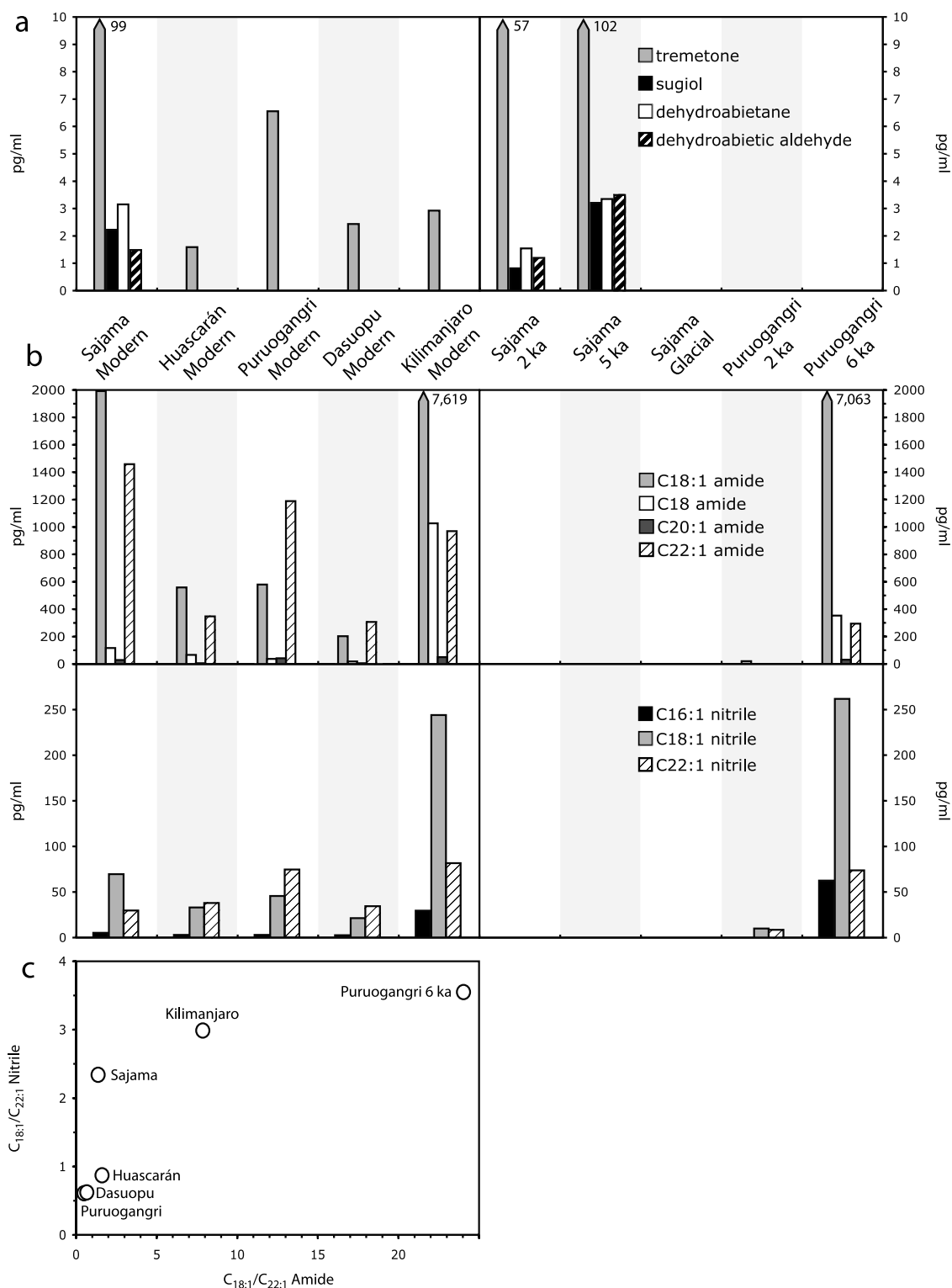


Figure 1. Biomarker abundances. Reported values are in pg/ml of ice and represent the mean of the results for all aliquots measured for each sample (blank levels and reproducibility are reported in Table S2). Results are shown for (a) biomass burning indicators and (b) alkyl amides and nitriles, for which a cross-plot of the (c) $C_{18:1}/C_{22:1}$ homologue ratios is provided.

compound occurs in all of the modern samples, unlike the conifer-derived diterpenoids, we attribute its presence to a more widespread vascular plant source.

[9] The observation that the modern Sajama sample was the only post-industrial one to contain dehydroabietane,

dehydroabietic aldehyde, and sugiol, and that it also exhibited the highest tremetone abundances, indicates that the Sajama ice cap is most favorably positioned to receive inputs of organic matter derived from fresh and combusted vascular plants, possibly due to regional climate conditions

or proximity to vegetation. Lower than average accumulation rates at the Sajama site during the Holocene [Thompson *et al.*, 1998] also may have aided in identification of these compounds in low volume samples. Inputs of plant combustion biomarkers to this core, and not Huascarán, are consistent with the drier climate conditions around Sajama, which could promote vegetation fires. Important to the development of our approach, the differences in aeolian organic carbon inputs to these ice fields suggest that they capture vegetation signals from limited geographic areas.

[10] Dehydroabietane, dehydroabietic aldehyde, sugiol, and tremetone were all detected in the two pre-industrial Holocene Sajama samples, but not in any other down-core sample, including glacial period Sajama ice. Abundances of these compounds are roughly similar to those in the modern Sajama sample, with approximately two times higher concentrations in the 5 ka than the 2 ka sample (Figure 1). Their presence in the Holocene samples and absence in glacial period ice is consistent with past climate trends at Sajama, for which proxy ice core records indicate that the mid to late Holocene climate was dry and warm, similar to present day conditions, whereas the last glacial period was much wetter and cooler [Thompson *et al.*, 1998]. The source specificity of these compounds and their absence in blanks (Table S2) identifies them as favorable ice core markers for biomass burning, and their consistency with aridity records suggests that they could be employed as an aridity proxy.

[11] Several factors could have contributed to the absence of vascular plant biomarkers in Sajama ice from the last glacial period, including changes in forest fire occurrence, differences in the type or areal extent of contributing vegetation, increased ice accumulation rates, degradation of organic matter, or changes in atmospheric circulation. The enhanced ice accumulation rates at Sajama during the last glacial period [Thompson *et al.*, 1998] would have the effect of diluting molecular species and the wet conditions may have suppressed fires. Both of these factors would result in diminished biomarker abundances, but are inseparable without the context of a continuous record. Additionally, photolytic or microbial degradation of organic matter within the ice or prior to deposition could have eliminated molecular species of interest [e.g., Kawamura *et al.*, 2001]. With the range of samples investigated in this study, separation of degradation and climate signals cannot be achieved, but development of high-resolution biomarker records may address these issues.

[12] Saturated and mono-unsaturated alkyl amides and nitriles (Figure S2) were major constituents of all the modern ice core samples, with $C_{18:1}$ and $C_{22:1}$ often as the most abundant homologues within both compound classes (Figure 1). Although laboratory blank levels precluded interpretation for some homologues, several longer-chain (C_{18} , $C_{20:1}$, and $C_{22:1}$) amides, the $C_{16:1}$ and $C_{22:1}$ nitriles, and *N,N*-dimethyloctanamide were detected in ice core samples but not in any blanks (Table S2). Additionally, reported $C_{18:1}$ nitrile abundances are considered robust for the modern Kilimanjaro and 6 ka Puruogangri samples, as are the $C_{18:1}$ amide results for these samples and modern Sajama ice.

[13] Potential sources of alkyl amides and nitriles in ice include thermally altered leaf wax fatty acids (i.e., through biomass burning), cooking byproducts [Simoneit *et al.*,

2003], and contamination from plastics [Grosjean and Logan, 2007], complicating their use as representative vegetation markers. Abas *et al.* [2004] identified a homologous series of alkyl nitriles in Malaysian atmospheric haze particulate samples and attributed their presence to biomass burning, and Oros and Simoneit [2001b] detected them in birch tree smoke. A hydrothermal pyrolysis study suggested that alkyl amides and nitriles can be produced through thermal alteration of fatty acids [Rushdi and Simoneit, 2004], such as those that occur in leaf waxes, as can shorter chain methyl alkamides [Simoneit *et al.*, 2003], such as *N,N*-dimethyloctanamide, which we detected in the modern ice core samples (not shown) from Sajama (140 pg/ml), Huascarán (3), Dasuopu (35), and Kilimanjaro (226), but not in any blanks (Table S2). These findings suggest that the *N*-bearing compounds we observed are derived at least partly from vegetation burning, having been generated through the condensation reaction scheme proposed by Rushdi and Simoneit [2004]. However, leachates from plastic core sleeves are a likely contaminant, so further investigation is warranted to constrain the source of these potentially useful biomarkers.

[14] Although similar alkyl amide and nitrile homologues were present in ice from different sites, their distribution varied with geographic location. These differences are depicted in a cross plot of the $C_{18:1}/C_{22:1}$ amide and nitrile ratios (Figure 1), in which Huascarán and the Asian ice cores exhibit similar compound distributions, while the modern Sajama and Kilimanjaro samples, as well as the Puruogangri 6 ka sample, each have more distinctive distributions. Given that the latter samples generally recorded the highest abundances of these compounds, their unique distributions may represent vegetation fire signals, whereas the signature in Huascarán and ice from the Asian sites may be indicative of contamination. Accordingly, the alkyl amide and nitrile homologue distributions in the Puruogangri 6 ka sample, which were very different from those in the modern one (Figure 1), would suggest contributions from burned vegetation in addition to plastic core sleeve contamination. The dry and cool conditions around 6 ka on the western Tibetan Plateau [Thompson *et al.*, 1997] would have been favorable for vegetation fires and reduced ice accumulation, possibly contributing to elevated levels of these compounds.

[15] The $C_{18:1}$ fatty acid homologue was detected in modern Sajama ice at a concentration of 2 ng/ml, but was not found in any blanks or in any other samples (Table S2). This compound, which is more labile than its saturated counterpart, is interpreted to be indicative of recent vascular plant or algal biogenesis [Abas *et al.*, 2004] and demonstrates the high preservation potential of a wide range of lipids in ice [e.g., Kawamura *et al.*, 1996]. It is not likely to have undergone aeolian transport over great distances or experienced long residence times in soil, as it would have been highly susceptible to oxidative degradation. The presence of the $C_{18:1}$ fatty acid homologue is thus consistent with a proximal vegetation biomarker source to the Sajama ice cap.

[16] A number of additional compounds potentially derived from vegetation fires or vascular plant leaf waxes were identified in the ice core samples, but occurred in abundances approaching or below blank levels (Table S2), preventing robust interpretation of results. For example, the

PAHs fluoranthene and pyrene were identified in many samples and achieved maximum concentrations of 2 and 8 pg/ml, respectively, in the modern Sajama sample, but were also abundant in laboratory blanks (1 pg/ml each). These are two of the major PAHs released during conifer combustion, but are not source-specific because they are also released through anthropogenic activities such as petroleum product and coal burning [Oros and Simoneit, 2001a]. *n*-Alkanes, which along with fatty acids occur plentifully in vascular plant leaf waxes [Eglinton and Hamilton, 1967], were abundant in the modern samples and were also observed in pre-industrial ice, but are not interpreted here due to high blank levels. Similarly, a number of fatty acid homologues (C_{12} – C_{16} and C_{18}) were identified in the ice core samples but are impacted to varying degrees by blank contamination (Table S2). These compounds may provide valuable organic geochemical and paleoclimate information in future studies pending mitigation of the blank contamination. The diterpenoids and tremetone, which are suggestive of biomass burning and fresh vascular plant inputs, were detected in ice core samples but were not observed in any blank, distinguishing them as the biomarkers of greatest utility in this study.

4. Conclusions

[17] The results of this investigation suggest that a range of biomarkers derived from vegetation fires and fresh vascular plant emissions are present in high-altitude ice in measurable quantities. The occurrence of the compounds observed in this study in recently deposited and mid-Holocene ice core samples supports the combined use of SBSE, TD, and GC/TOF-MS for investigation of organic matter preserved in high-altitude ice fields, and the reduced sample volumes (≤ 30 ml) afforded by these methods is compatible with the future generation of high-resolution, multi-molecular stratigraphic records. Differences between the types and distributions of biomarkers observed for each of the sampling sites suggest that inputs of organic matter track regional vegetation and climate variables and could be used to construct stratigraphic records pertinent to constrained geographical areas. Furthermore, changes in the biomarker composition of Sajama ice over time that are consistent with independent aridity records support the use of our methods to investigate temporal variability in forest fire occurrence. To our knowledge, this is the first study to apply SBSE, TD, and GC/TOF-MS to ice core investigations, as well as the first to identify the diterpenoid compounds we observed in this medium. Through their specificity, these compounds in particular represent the greatest potential for use as forest fire and aridity proxies.

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