

## Hydrogen, lithium and boron in mantle-derived olivine: The role of coupled substitutions

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### ABSTRACT

We report major element, boron, lithium, and water (present as structurally bound hydroxyl groups) contents for a suite of ten mantle-derived olivine crystals, measured by electron microprobe, secondary ion mass spectrometry, and Fourier-transform infrared spectroscopy. Water measurements are based on re-analysis and/or re-processing of data previously reported in the literature. Our data allows us to assess the role of substitutions between these elements, and in particular provide a means to test the role of the coupled substitution  $B(F,OH)Si_{1-x}O_{1-x}$  in controlling the boron and water contents of mantle olivine.

Analyzed olivines have lithium, boron, and water concentrations of 0.9–7.8 and 0.01–67, and 0.8–61 ppm (by weight), respectively. One olivine from Kingiti, Tanzania (possibly derived from metasomatized peridotite) is anomalous, with boron and lithium contents of 67 and 7.8 ppm, respectively. The remaining olivine samples have lithium and boron contents below 3 and 1 ppm, respectively. Although lithium, boron, and water contents vary substantially, their cation proportions are not strongly correlated, arguing against simple coupled substitutions involving these elements. Importantly, the incorporation of boron and water in olivine by the  $B(F,OH)Si_{1-x}O_{1-x}$  substitution does not appear to be a universal feature of mantle olivine, although it may be significant in those with the highest boron contents.

Our data also support suggestions that olivine may be an important reservoir for hydrogen, lithium, and boron in the lithospheric and upper asthenospheric mantle, and may thus play a key role in the geochemical cycling of these elements within the mantle, and between the mantle and crust.

### INTRODUCTION

There is considerable evidence to suggest that substantial water may be contained within the earth's mantle, structurally bound (as hydroxyl groups) within nominally anhydrous mantle phases (e.g., olivine, garnet, clinopyroxene; Miller et al. 1987; Bell and Rossman 1992; Kurosawa et al. 1997; Jamtveit et al. 2001). The presence of water within these minerals provides an important reservoir for water within the mantle (Thompson 1992), and likely exerts a major influence on important mineral physical properties (Mackwell et al. 1985; Karatao et al. 1986). The water contents of olivine are of particular interest, as this mineral constitutes the major modal proportion of the lithospheric and upper asthenospheric mantle (e.g., Menzies 1990; Bernstein et al. 1998). Measurements to date indicate that typical water contents of mantle olivines and those that crystallize from mantle-derived melts range between ~1–60 ppm H<sub>2</sub>O (Miller et al. 1987; Bell and Rossman 1992; Kurosawa et al. 1997; Jamtveit et al. 2001; Table 1). Olivines from crustal rocks show a wider range of water contents (up to ~700 ppm H<sub>2</sub>O; Miller et al. 1987; Sykes et al. 1994).

To date, the specific mechanisms by which hydroxyl is incorporated into olivine remain unclear. Kurosawa et al. (1997) observed a broad correlation between the hydrogen

content of olivine and trivalent cation contents in garnet peridotites and suggested that coupled substitution of hydroxyl may occur in oxygen positions adjacent to M site vacancies. However, similar correlations were not observed in olivine from spinel peridotite, suggesting that such a mechanism may not be universal. Sykes et al. (1994) noted that olivine from the Tayozhnoye iron deposit, Siberia, Russia, that contains substantial B<sub>2</sub>O<sub>3</sub> (1.35 wt%) also contained high H<sub>2</sub>O (714 ppm from the preferred calibration of Sykes et al. 1994) and fluorine (0.33–0.55 wt%), and suggested that hydroxyl is incorporated into the olivine structure by the coupled charge-balanced substitution  $B(F,OH)Si_{1-x}O_{1-x}$  (Christ 1965; Grew et al. 1991; Sykes et al. 1994; Grew 1996). Although the Tayozhnoye olivine formed during crustal metamorphism, Sykes et al. (1994) suggested that this substitution could also provide a means by which significant structurally-bound boron and hydrogen may be stored in mantle olivine, and thus may play an important role in the volatile element systematics of the upper mantle—although to date there has been little data with which to test this hypothesis. To directly address the role of the  $B(F,OH)Si_{1-x}O_{1-x}$  substitution within mantle olivine we report the concentrations of boron and water, as well as lithium, from a suite of olivine crystals from eclogitic, peridotitic, and basaltic rocks.

Although the olivine-liquid partitioning of lithium and boron are comparatively well known from experimental studies (e.g., Chaussidon and Libourel 1993; Brenan et al. 1998; Taura et al. 1998) and data for the lithium content of peridot-

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**TABLE 1.** Major element, lithium, boron and hydrogen contents of analyzed olivine

Sample number*	1	3	9	34	11	14	17	21	19	15
Occurrence	Eclogite	Eclogite	Kimberlite Xenolith	Kimberlite Xenolith	Basalt Xenolith	Basalt Xenolith	Basalt Xenocryst?	Basalt Xenocryst	Basalt Phenocryst?	Leucitite†
Location	Norway	Norway	Monastery, South Africa	Kimberley, South Africa	Emali, Kenya	Toowoomba, Australia	Kingiti, Tanzania	Hebei Pr. China	Noisy Mitsio, Madagascar	Vesuvius, Italy
Reference‡	1,2	1,2	1,3	1	1,5,6	1	1	1,4	1,7	1
MgO	51.49	51.24	50.34	50.60	50.08		50.54	49.38		46.61
SiO <sub>2</sub>	41.62	41.51	41.25	41.53	41.24		41.33	40.89		40.34
MnO	0.10	0.10	0.11	0.10	0.13		0.10	0.12		0.21
FeO	6.97	7.04	7.83	7.27	7.79		7.40	8.54		12.14
NiO	0.38	0.36	0.38	0.52	0.42		0.36	0.38		0.17
CaO	0.002	0.001	0.004	0.046	0.005		0.029	0.025		0.303
P <sub>2</sub> O <sub>5</sub>	0.011	0.012	0.016	0.028	0.030		0.013	0.019		0.046
Total	100.57	100.26	99.93	100.09	99.70		99.77	99.35		99.82
Forsterite (%)	92.94	92.84	91.97	92.54	91.97		92.41	91.15		87.25
H (ppm) §	2.2, 2.3	2.6, 1.4	6.8	16.5#, 3.2**	3.8	0.09	1.8	0.7	0.8	5.3
H <sub>2</sub> O (ppm)	20	23	61	147, 29	34	0.8	16	6.3	7.1	47
Li (ppm)	1.6	1.2	0.9	2.3	0.9	1.1	7.8, 7.7††	0.8	1.5	2.7
B (ppm)	0.41	0.30	0.15	0.06	0.01	0.03	65, 67††	0.02	0.03	0.28
<b>Cation proportions (on the basis of four O atoms) ††</b>										
SiO <sub>2</sub>	1.0015	1.0022	1.0029	1.0055	1.0049		1.0040	1.0035		1.0020
FeO	0.1403	0.1421	0.1592	0.1472	0.1588		0.1503	0.1753		0.2522
NiO	0.0074	0.0070	0.0074	0.0101	0.0082		0.0070	0.0075		0.0034
MnO	0.0020	0.0020	0.0023	0.0021	0.0027		0.0021	0.0025		0.0044
MgO	1.8464	1.8436	1.8240	1.8259	1.8187		1.8298	1.8060		1.7254
CaO	5.16E-05	2.58E-05	1.03E-04	1.19E-03	1.29E-04		7.48E-04	6.57E-04		7.81E-03
P <sub>2</sub> O <sub>5</sub>	2.24E-04	2.44E-04	3.26E-04	5.70E-04	6.11E-04		2.65E-04	3.87E-04		9.37E-04
Total	2.9982	2.9975	2.9966	2.9936	2.9941		2.9955	2.9959		2.9963
H	2.18E-04	2.58E-04	6.75E-04	3.17E-04	3.77E-04	8.93E-06	1.79E-04	6.94E-05	7.94E-05	5.26E-04
Li	3.33E-05	2.51E-05	1.89E-05	4.82E-05	1.90E-05	2.28E-05	1.64E-04	1.70E-05	3.11E-05	5.81E-05
B	5.48E-06	4.03E-06	2.03E-06	8.07E-07	1.35E-07	3.99E-07	8.78E-04	2.73E-07	3.99E-07	3.87E-06

Notes: Unless shown otherwise all concentrations are in weight percent.

\* Sample number from (Miller et al. 1987).

† 1776 eruption of Vesuvius.

‡ References: 1 = Miller et al. (1987), 2 = Brueckner (1977); 3 = Whitelock (1973), 4 = Keller and Fuquan (1986), 5 = Suwa et al. (1975), 6 = Bank and Saul (1972), Lacroix (1922).

§ Hydrogen data recalculated from the spectra of Miller et al. (1987) using the olivine specific calibration of Bell et al. (*in preparation*) except for samples 1 and 3.

|| Original water content as reported by Miller et al. (1987).

# With molecular water.

\*\* Without molecular water.

†† Duplicate analysis.

‡‡ Cation proportions for olivine 14 and 19 calculated using an olivine composition of 92% Forsterite (SiO<sub>2</sub> = 41.7, MgO = 50.5, FeO = 7.8).

ite olivines have recently become available (Kurosawa et al. 1997; Seitz and Woodland 2000), the boron contents of naturally-occurring mantle-derived olivine samples are less well-known. Early work by Seitz (1973) and Steele et al. (1981) suggested that mantle olivines may have boron contents up to ~0.3 ppm, and Chaussidon and Libourel (1993) reported boron contents of ~0.15 ppm in olivine crystals produced during experimental melting of natural peridotite compositions (with ~1 ppm boron). Thus, although boron may be a common trace phase in mantle olivine at the 0.1–1 ppm level, it remains unclear whether mantle olivine may contain sufficient boron (up to ~80 ppm) required to explain the range of water contents measured in mantle olivines. **{The preceding sentence was quite confusing. Please check that modification has not changed the sense.}** Lithium appears to be more compatible than boron within mantle olivine (Brenan et al. 1998; Taura et al. 1998) and is generally present in concentrations between 1–5 ppm in both peridotitic olivines (Kurosawa et al. 1997; Seitz and Woodland 2000) and those that crystallized from island arc and ocean island basalts (Kent unpublished data 1998). Seitz and Woodland (2000) also sug-

gested that the lithium contents of olivine and other minerals from peridotite xenoliths may be used as an indicator of magmatic and metasomatic mantle processes.

## SAMPLES

The olivine crystals we have analyzed are a subset of those analyzed for water content by Miller et al. (1987) and derive from eclogitic ( $n = 2$ ), kimberlitic (2), and basaltic (6) rocks. Details of these samples are given in Miller et al. (1987) and references therein and olivine parageneses are summarized in Table 1. Samples consist of near-gem quality olivine crystals, chosen to minimize the potential effect of small inclusions on measured hydroxyl, lithium, and boron contents, and thus are ideal for a study of coupled substitution mechanisms of low-abundance trace elements (that may be disproportionately affected by the presence of small inclusions).

## EXPERIMENTAL METHODS

MgO, SiO<sub>2</sub>, MnO, FeO (measured as total Fe), NiO, CaO, and P<sub>2</sub>O<sub>5</sub> contents of the olivine samples were analyzed by electron microprobe at the California Institute of Technology

using a JEOL-733 Superprobe with an accelerating voltage of 15 kV and an electron beam current of 15 nA. Elemental concentrations were calculated via reference to a suite of mineral and oxide standards. The reported compositions of each olivine sample represents the average of four separate analyses, with the external reproducibility (1 standard deviation) of major elements compositions being typically <1% for MgO, SiO<sub>2</sub>, and FeO; <8% for NiO and MnO, and <25% for CaO and P<sub>2</sub>O<sub>5</sub>. Fluorine contents for all olivine crystals were below the detection limit (~0.01 wt%).

Lithium and boron contents were analyzed by secondary ion mass spectrometry (SIMS) using a modified Cameca 3f ion probe at Lawrence Livermore National Laboratory. For analysis, polished surfaces of olivine samples were coated with ~100 Å gold to reduce surface charging. General analytical schemes for measurement of boron and lithium concentrations by SIMS are discussed by Ottolini et al. (1993), Hervig (1996), and Kent et al. (1999a). Analyses were made with a 10 nA primary beam (~30 mm diameter) of <sup>16</sup>O<sup>-</sup> ions accelerated at 12.5 kV. For analysis a 30 mm aperture was inserted in the sample image plane. Sputtered ions were accelerated at a nominal 4.5 kV through a double-focusing mass spectrometer, and selected ion beams were measured with an electron multiplier. To suppress isobaric molecular species and minimize matrix effects, an energy offset of -100 ± 30 eV was applied (relative to the voltage at which the intensity of <sup>16</sup>O<sup>-</sup> dropped to 10% of its maximum value on the low energy side of the energy distribution) and a mass-resolving power of ~650 was used for all analyses. Each analysis consisted of 10 mass spectrometer cycles with the count times for an individual cycle of 1, 5, and 20s for <sup>30</sup>Si<sup>+</sup>, <sup>7</sup>Li<sup>+</sup>, and <sup>11</sup>B<sup>+</sup>, respectively. Surface contamination can be an important factor in light element (particularly boron) analyses and to remove this, a ~100 × 100 mm area centered on the analysis spot was rastered with the ion beam for 5–10 minutes prior to analysis. After rastering, lithium and boron blanks measured on gold-coated semiconductor grade silicon were ~0.002 and 0.01 ppm.

Measured <sup>7</sup>Li<sup>+</sup>/<sup>30</sup>Si<sup>+</sup> and <sup>11</sup>B<sup>+</sup>/<sup>30</sup>Si<sup>+</sup> ratios were converted to parts per million lithium and boron using sensitivity factors determined from measurement of the NBS 610, 612, and 614 standard glasses. Although these glasses have higher SiO<sub>2</sub> contents (~70 wt%) than olivine, indications from the literature (e.g., Hervig 1996) and measurements by us of basaltic glasses (Kent et al. 1999a, 1999b) indicate that, at the energy offsets used here, matrix-related variations in lithium and boron sensitivity factors are minimal. The long term 1S reproducibility of repeated lithium and boron measurements on standard glasses is ±8%.

Water contents for all samples were determined by Fourier-transform infrared spectroscopy (FTIR). For eight olivine samples water contents were recalculated from the original data of Miller et al. (1987) using the specific calibration of the olivine spectrum (of Bell et al., in preparation). For two samples (1 and 3), infrared spectra were re-acquired with a Nicolet Magna 860 FTIR using a LiIO<sub>3</sub> crystal polarizer and a room-temperature DTGS (Deuterated TriGlycine Sulphate) detector. This newer instrumentation required less material

to be sampled, thus further minimizing the potential contribution of inclusions. In the spectra of samples, 15 and 21 contributions from ice in the cryogenic detection system were removed before the integration was performed by subtracting a standard ice pattern from the sample spectrum. Contributions from molecular water in inclusions or cracks were also removed from sample spectra. To quantify water contents, the Nicolet Omnic software package was used to manually generate a background modeled and patterned after the spectra of dehydrated San Carlos olivine and synthetic Mg<sub>2</sub>SiO<sub>4</sub>. Before integration of the spectra of samples with lower water contents (the majority), this background was subtracted from the experimental spectrum. Eclogitic olivines from Norway (numbers 1 and 3 of Miller et al. 1987; Table 1) were also processed to remove the serpentine bands near 3700 cm<sup>-1</sup> (discussed by Miller et al. 1987) before integration. The spectrum of sample 34 was processed both before and after a broad underlying band was removed (Table 1). This band is presumed to be from exsolved molecular water (Miller et al. 1987).

## RESULTS AND DISCUSSION

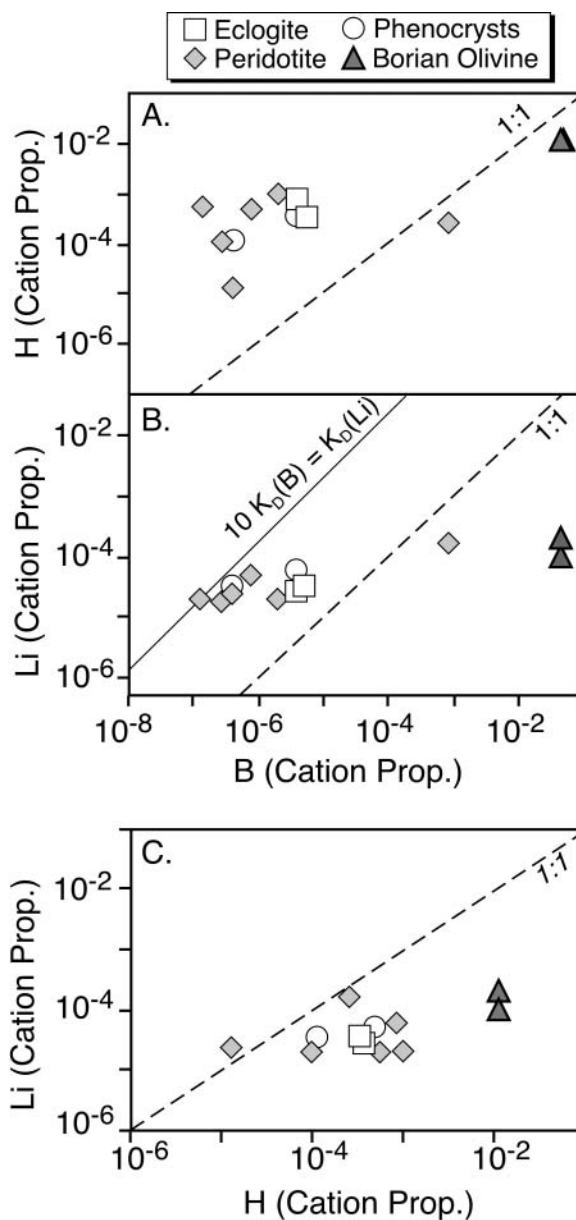
Lithium, boron, and hydrogen (present as bound hydroxyl groups) contents of the analyzed olivine samples are shown in Table 1 and range between 0.9–7.8 and 0.01–67, and 0.09–6.8 ppm (0.8–61 ppm water), respectively. The sample from Kingiti, Tanzania (number 17) is clearly anomalous having substantially higher boron and lithium contents (65, 7.8 ppm) than other olivines measured. The remaining samples have boron contents that are less than 1 ppm, with the highest concentrations in eclogite and phenocryst-derived olivines (Table 1), suggesting that these formed in more boron-rich environments, presumably in equilibrium with a metamorphic fluid or basaltic melt phase (e.g., Leeman and Sisson 1996; Woodford et al. 2001). With the exception again of the Kingiti olivine, the lithium contents cover a broadly similar range to that reported in other studies of the lithium content of olivine (~1–5 ppm; Kurosawa et al. 1997; Seitz and Woodland 2000), with no clear differences between olivines of differing origin.

As noted above, one sample from Kingiti, Tanzania, has anomalously high boron content. The lithium content of this sample (7.8 ppm) is also higher than the other olivine crystals analyzed (as well as the lithium contents of other mantle olivines reported in the literature), although the measured water content is within the normal range for mantle olivine (Table 1). Repeat measurements confirm the higher boron and lithium contents (Table 1), however the reason for anomalously high boron and lithium is unclear. The exact paragenesis of this olivine (phenocrystic or xenocryst) is unfortunately uncertain, as it was obtained directly from a mineral dealer, although the high forsterite and NiO contents and the low CaO content are consistent with mantle peridotite (Table 1). Furthermore, it is unlikely that this olivine either crystallized from (or equilibrated with) a melt, as the high forsterite content and known olivine-melt partitioning of boron requires a primitive melt containing at least ~1300 ppm boron (using  $K_{\text{Dsolid-melt}} = 0.05$ ; Chaussidon and Libourel 1993; Brenan et al. 1998; Taura et al. 1998), which is considerably greater than

the  $\ll 100$  ppm boron contents typical of primitive basalts, even those from subduction zones (e.g., Chaussidon and Albert 1994; Gurenko and Chaussidon 1995; Leeman and Sisson 1996; Kent et al. 1999a, 1999b). The high measured boron contents in this olivine suggest that, at least in some locales, mantle olivines may contain  $\gg 10$  ppm boron, although further work is required to ascertain how common such high-boron olivines are within the mantle. The high lithium content of this sample suggests that it derives from metasomatized mantle peridotite (e.g., Seitz and Woodland 2000), and this may also explain the high boron contents, as metasomatizing mantle fluids would be expected to be enriched in boron (due to the incompatible behavior of boron during both melt-solid and melt-fluid reactions; e.g., Leeman and Sisson 1996).

Our data also allow us to specifically examine the role of the  $B(F,OH)Si_{1-x}O_{1-x}$  coupled substitution in controlling the boron and hydroxyl contents of mantle olivine. In Figure 1a we compare the calculated cation proportions of boron with hydrogen in the analyzed samples. The majority of mantle-derived olivines that we measured show distinct enrichments in hydrogen over boron that represent large departures (up to several orders of magnitude) from the 1:1 trend expected from the  $B(F,OH)Si_{1-x}O_{1-x}$  substitution (Fig. 1a). Measured boron and hydroxyl contents of the analyzed samples are not strongly correlated (although there is a tendency for the most boron-rich olivines to also be relatively water-rich). The departure of our data from the 1:1 atomic trend cannot be explained by additional fluorine (which in any case was not detected at levels greater than 0.01 wt% in our samples), as this would move them even further from the 1:1 trend (as hydrogen contents represent minimum estimates for the total hydrogen + fluorine; Fig. 1a). Our data therefore suggests that boron and water are not universally accommodated within mantle olivine by the  $B(F,OH)Si_{1-x}O_{1-x}$  substitution. However, both the anomalously boron-rich olivine from Kingiti (number 17) and the Tayozhnoye borian olivine of Grew et al. (1991) and Sykes et al. (1994) plot close to the 1:1 trend, suggesting that, at relatively high boron contents (more than several 10s ppm), the  $B(F,OH)Si_{1-x}O_{1-x}$  substitution may be the dominant mechanism for boron and water incorporation into the olivine structure (Sykes et al. 1994; Grew 1996). One explanation for the apparent excess water contents (i.e., those above the 1:1 line in Fig. 1a) observed in low-water olivine samples may be the presence of exsolved nanometer-size hydrous olivine  $[(Mg_{1-y}Fe_y^{2+})_{2-x}SiO_4H_{2x}]$  zones within individual samples, as recently observed by Khisina and Wirth (2002).

On the log scales used in our plots, the concentrations of boron, lithium, and hydrogen all appear to be weakly correlated over several orders of magnitude (Figs. 1a–1c), although these trends are all significantly different to those expected for simple 1:1 coupled substitutions. It is unclear as to whether these trends reflect the co-substitutions of these elements, or overall positive co-variation between lithium, boron, and hydrogen in the different environments where mantle olivines form (such that boron-rich environments are also lithium and water-rich and vice versa). If the latter is the case then we also note that the trend defined by lithium and boron (Fig. 1a) departs significantly from the trend expected from the



**FIGURE 1.** Cation proportion plots for measured trace element abundances in olivine from this study, as well as for the Tayozhnoye borian olivine from Grew et al. (1991) and Sykes et al. (1994): (a) boron vs. hydrogen; (b) boron vs. lithium; (c) hydrogen vs. lithium. Dashed lines shows expected trend for 1:1 atomic substitutions between plotted elements and the solid line in (b) represent the partitioning of boron and lithium into olivine following the relationship  $10 K_b(B) = K_b(Li)$ , which represents the highest ratio of boron to lithium melt-liquid partition coefficients measured by Taura et al. (1998).

relative partitioning of boron and lithium between melt and olivine (e.g., Brenan et al. 1998; Taura et al. 1998).

Our data also provide further confirmation that olivine can accommodate small, but significant, amounts of boron, lithium, and water within the mantle (e.g., Miller et al. 1987; Bell and Rossman 1992; Kurosawa et al. 1997; Seitz and

Woodland 2000) and, in particular, suggest that olivine is an important reservoir for boron (Leeman and Sisson 1996) within lithospheric and upper asthenospheric mantle lithologies. Given the range of concentrations of boron in olivine reported herein and the general modal dominance of olivine in most lithospheric and upper asthenospheric mantle rocks (typically >50–70 modal percent; Menzies 1990; Bernstein et al. 1998), olivine could well host the majority of the boron estimated to occur within depleted and primitive mantle compositions (between ~0.3–0.01 ppm; e.g., Leeman and Sisson 1996). Olivine may be particularly important as a host mineral in environments that are inherently boron-rich, such as mantle regions that have been metasomatized or the enriched portions of the mantle wedge above subducting slabs, and/or if exceptionally boron-rich olivines, such as that from Kingiti, are more widespread in mantle-derived rocks than previously considered.

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