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NOTE

Sequential sample reservoirs for Itrax-XRF analysis of discrete samples

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Abstract Geochemical analysis of sediment samples can be used to characterize between- and within-lake variability and provide insights into lake chemistry, depositional processes and contamination sources. The number of samples for geochemical studies is restricted by cost, sample volume required, and the destructive nature of inductively coupled plasma mass spectrometry, instrumental neutron activation analysis, or wavelength dispersive x-ray fluorescence. Core scanners that incorporate energy dispersive x-ray fluorescence spectrometry, such as the Cox Itrax-XRF core scanner, have high throughput and can be used to produce high-quality geochemical datasets at low cost without destroying sample material. Here we describe a new analysis vessel that enables rapid, non-destructive Itrax-XRF analysis of discrete sediment samples.

Keywords Itrax-XRF · XRF core scanners · Surface sample · Geochemistry · Spatial resolution · Soil samples · X-ray fluorescence

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Introduction

Synoptic limnological studies can be used to characterize the range of lake environmental variability on regional and local scales. These studies provide background information essential for interpretation of paleolimnological records (Pienitz et al. 1997; Rühland and Smol 1998; Rühland et al. 2003) and characterization of water quality and other parameters (Patterson et al. 2012; Roe et al. 2010). Multi-station, intra-lake studies have proven that no single site can fully represent conditions throughout a lake (Engstrom and Rose 2013). Understanding the mechanisms that underlie within-lake spatial environmental heterogeneity can shed light on depositional processes (Dietze et al. 2012) and point-source contamination (Li et al. 2013). The primary limitations to carrying out detailed multi-station, intra-lake studies are cost, sample volume requirements and the destructive nature of conventional techniques, such as inductively

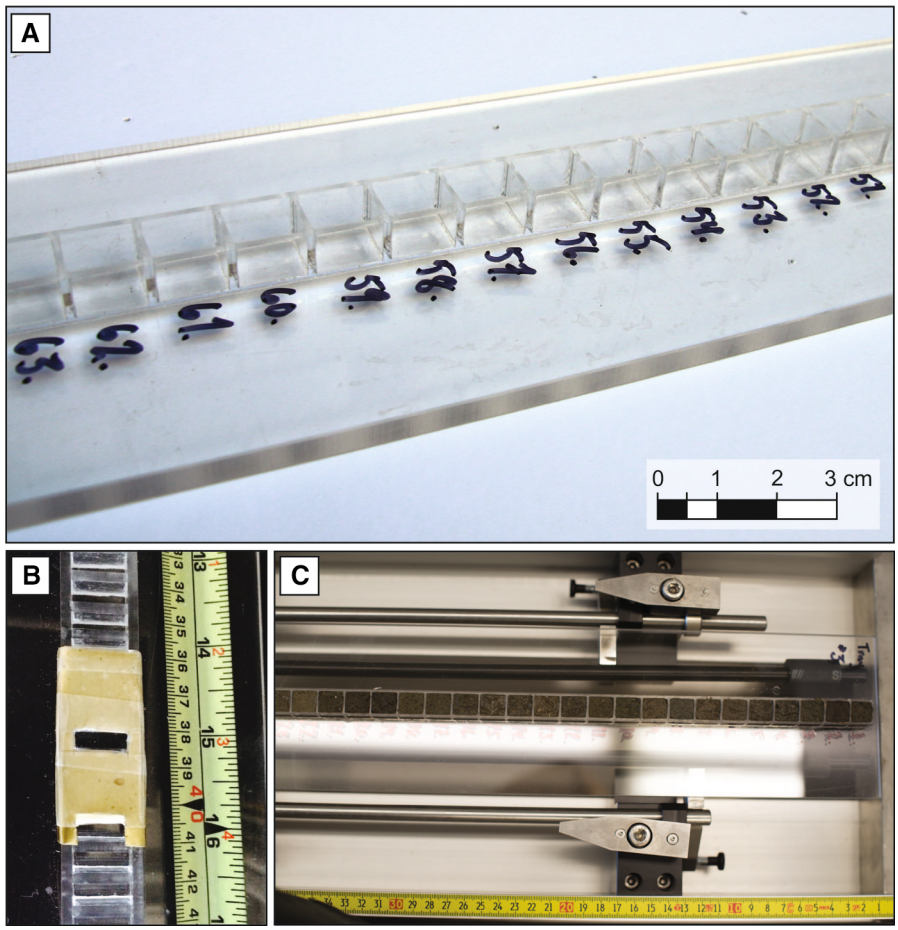


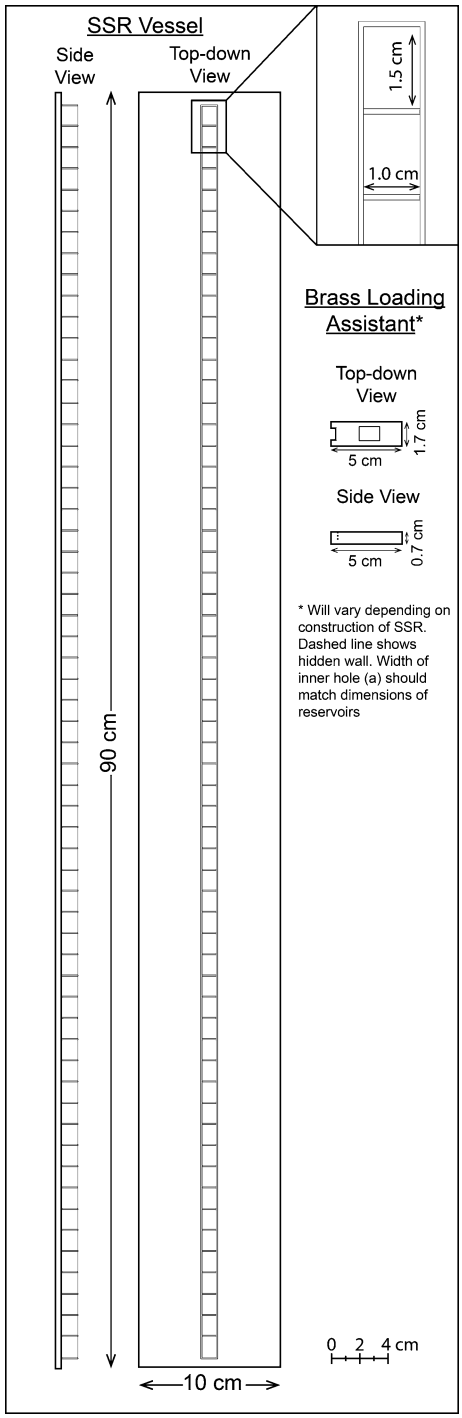
Fig. 1 **a** Oblique view of the SSR showing detailed 3D structure. **b** SSR with shorter reservoirs, used when sample material is limited. Pictured also is the brass cover to minimize cross-contamination and streamline loading. **c** Close-up of SSR showing sediment in compartments, forming a continuous "core" for analysis. Color figure available online

coupled plasma mass spectrometry (ICP-MS), wavelength dispersive x-ray fluorescence (WD-XRF), and instrumental neutron activation analysis (INAA).

Core scanners that incorporate energy-dispersive x-ray fluorescence spectrometry (ED-XRF), such as the Cox Itrax-XRF core scanner, are being used increasingly in the environmental sciences. Core scanners have improved the ability of researchers to carry out rapid, inexpensive, and non-destructive assessment of environmental variables in cores. The 0.1-mm scanning resolution that can be obtained with Itrax-XRF core analysis means that sub-annual-scale temporal resolution is possible in many cases (Rothwell and Croudace 2015). Adapting the Itrax-XRF instrument for geochemical analysis of discrete sediment samples has the potential to increase the capacity to analyze samples non-destructively and inexpensively by at least an order of magnitude, e.g. from tens to hundreds. This new tool can thus dramatically increase spatial coverage in studies that use discrete sediment samples, such as lacustrine sediment–water interface samples, soils in archaeological contexts, or even subsamples from previously sampled or degraded sediment cores that are no longer suitable for conventional core scanning. Here we: (1) describe a vessel that enables Itrax-XRF analysis of discrete sediment samples, (2) discuss pre-analysis and post-analysis protocols required for analysis carried out using the vessel, and (3) provide an example of its use.

Analysis of sediment with the Itrax-XRF

The Itrax-XRF core scanner is designed to record continuous geochemical changes throughout the length of a dewatered sediment core, which can even have been left in the original, split core barrel. In order



◀**Fig. 2** Schematic diagram of the SSR with larger wells and the brass loader assistant used to minimize cross-contamination and facilitate rapid loading of the SSR. Device is 90 cm long by 10 cm wide. *Inset* shows magnified reservoirs with dimensions 1.0 cm wide by 1.5 cm long by 1.0 cm deep. Brass loader is 5 cm long by 1.7 cm wide, with the inner hole having the same dimensions as the reservoirs (1.5 × 1.0 cm). The brass loader assistant has folded sides to hold it in place and a small fold on the front to hook the device in place on a subsequent reservoir (*dashed line* on side view). The brass loader assistant should be long enough to cover at least one previous and subsequent reservoir

to enable analysis of discrete sediment samples with the Itrax-XRF, sediment samples must be arranged to form a "continuous" record in a de-watered form, thus simulating a conventional sediment core.

Description of the Itrax sequential sample reservoir (SSR) vessel

The Itrax sequential sample reservoir (SSR) described here is comprised of connected acrylic compartments, 1.5 × 1 × 1 cm, aligned down the center of a clear acrylic base, 10 cm wide by 90 cm long (Figs. 1a, 2). This length allows two full vessels to be loaded sequentially into the Itrax for analysis. If sample volume is restricted, smaller wells can be used (1.5 × 0.5 × 1 cm; Fig. 1b). The SSR accommodates 59 compartments in a configuration that mimics a conventional sediment core. Acrylic was selected for construction material because of its low cost, durability, and ease of assembly. Acrylic was used instead of commonly available white PVC, which during prototype testing was found to contain high amounts of Ti and Zn that are used to color the plastic and can potentially contaminate analytical results.

Operation of the SSR vessel

Water content in sediment–water interface samples is often very high, in some cases >90%. High water content in samples could potentially increase attenuation of the XRF signal (Tjallingii et al. 2007). Sediment that is too wet may also bleed over into adjacent compartments during loading of the vessel and result in cross-contamination. To minimize this problem, we recommend that samples be centrifuged, the supernatant discarded, and sediment plugs dried at room temperature until they reach the consistency of moist paste. Alternatively, supernatant can be retained and samples dried at room temperature if there is concern about the loss of soluble elements in the

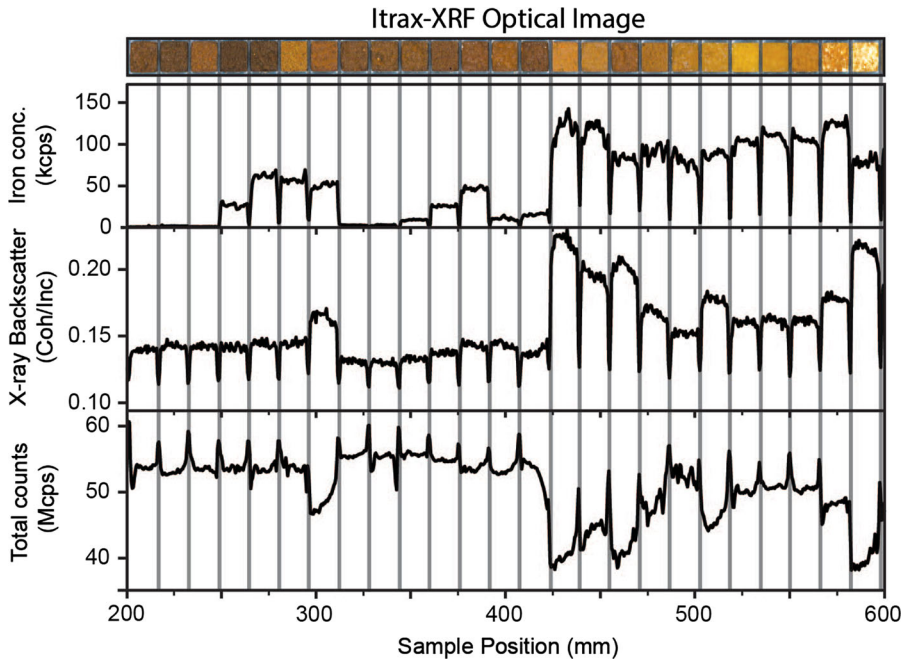


Fig. 3 Line graphs of changing iron content in thousands of counts per second (kcps; *top graph*), the ratio of coherent to incoherent x-ray backscatter (*middle graph*), and total counts in millions of counts per second (Mcps; *lower graph*) with increase in sample position being analyzed (mm). The photo at the *top* of the figure shows the optical image of the SSR device loaded with sediment taken by the Itrax core scanner. Abrupt shifts represent analysis of acrylic between compartments of the SSR vessel (indicated in *grey*). These intervals should be removed before further statistical analysis. Colour figure available online

water. The sediment, however, should not be too dry, as there is risk of airborne cross-contamination between samples, and oxidation of sensitive materials that may be subsequently analyzed (e.g. microfossils). By drying to a moist paste, samples will be more comparable to the sediment consistency and content of conventional cores.

Before loading samples into the SSR, material should be homogenized with a spatula. When loading samples into the SSR, it is necessary to pack the sediment using a spatula, to ensure there are no air pockets at the bottom of the reservoir. Air pockets can result in the settling of sediment during analysis, creating uneven surface topography. Abrupt changes in surface topography can cause "data shadows" in areas where depressions or protrusions exist because the Itrax-XRF detector automatically adjusts its position to ensure it does not make contact with the sediment surface. Sediment should be allowed to settle overnight and more should be added, if necessary, to ensure the sample surface is flush with the top of the SSR. A brass cover coated with cellophane tape, which has an opening the same dimensions as one reservoir, can be used to block previously loaded and subsequent reservoirs to prevent cross-contamination and speed the loading process (Figs. 1b, 2). Before analysis, the surface of sediment samples loaded into the SSR should be smooth and flat, as the Itrax-XRF detector must remain at a constant distance from the sample surface and even minor topographic artifacts may induce errors in analysis. To ensure that the plastic dividers between reservoirs are easily identifiable, they should be cleaned before analysis.

Once sediment samples are loaded into the SSR, it is fitted to the rails of the Itrax-XRF (Fig. 1c). The rails of the Itrax-XRF should be placed at their highest setting and rubber-tubing shims should be added to bring the SSR close to the XRF detector. The compartments must be aligned straight down the center of the rails and taped in place as the XRF beam follows a 2-mm-wide path down the center of the track during analysis. During the surface scan prior to analysis, centering of the sampler can be checked and corrected, if necessary. Once properly centered, analysis can proceed using standard Itrax operating procedures (Croudace et al. 2006).

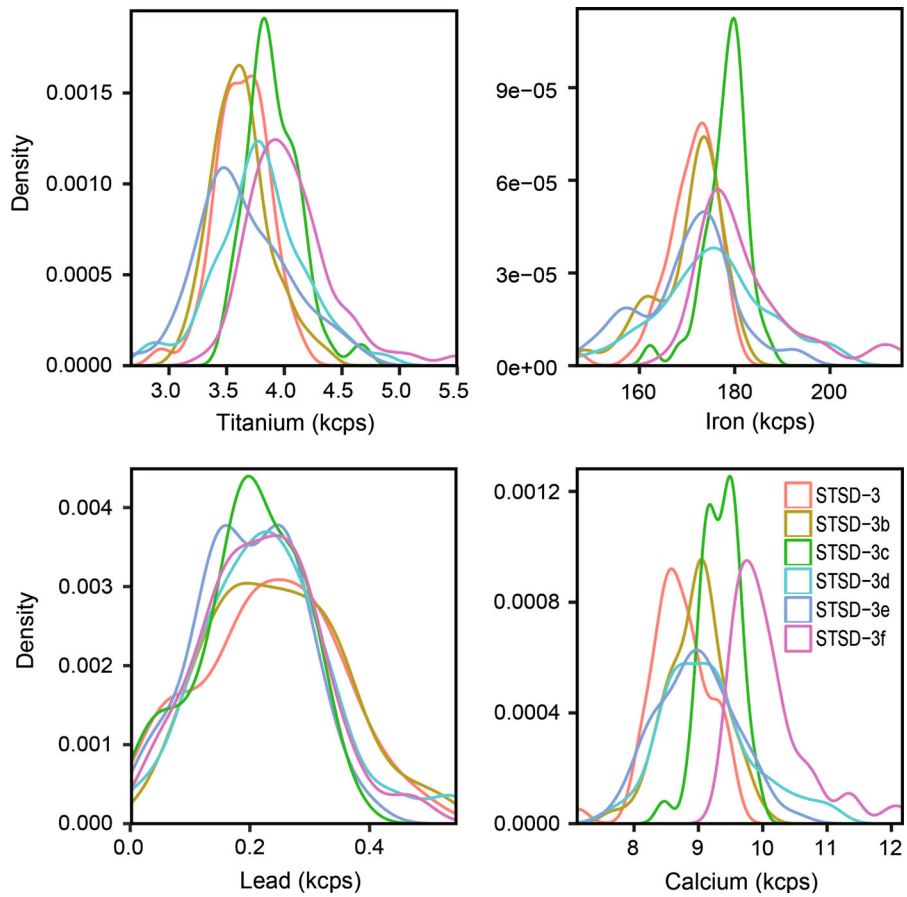


Fig. 4 Density plots for replicate scans of powdered Geological Survey of Canada Stream Sediment Standard-3 (STSD-3) for calcium, lead, titanium and iron measured in thousands of counts per second (kcps). STSD-3 was added at the start and end of the SSR device when analyzing Harvey Lake surface samples. Elements displayed span lighter elements (Ca, Ti) that have poor detection relative to heavier elements that have better detection (Fe, Pb) by the Itrax-XRF, using a Mo-anode. Colour figure available online

Post analysis data interpretation

Prior to interpreting results, sample measurements must be distinguished from measurements of the acrylic borders that separate the reservoirs. Simple line graphs plotted from the Itrax-XRF results will reveal analytical results associated with the acrylic. The acrylic comprising the SSR compartment walls can be identified readily on the basis of: (1) a significant shift in the total number of counts for a given interval, as the acrylic generally has a density different from sediment and may increase x-ray scatter because of the abundance of lighter elements in acrylic; (2) a major decrease in abundant element concentrations (Fe has proven to be a useful marker in our research); (3) a considerable decrease in the ratio of coherent/incoherent backscatter, which is a proxy for mean atomic number (Boyle et al. 2015); and (4) knowledge of the length of each compartment (Fig. 3). Once identified, the SSR compartment-wall data can be removed from the results. We also recommend removing analysis results collected within 1 mm of the acrylic edge, to minimize possible boundary effects. The mean square error (MSE) of measurements made by the Itrax-XRF core scanner can be used to assess whether data were influenced by air pockets close to the compartment walls, caused by settling of sediment, and data points identified as outliers can be removed accordingly. At a sampling resolution of 0.2 mm, a scan of each sample compartment will provide 75 data points in 18.75 min at an exposure time of 15 s. Itrax-XRF core scanners allow the user to adjust count time and resolution to increase the speed or accuracy and precision of geochemical results. Summary statistics (e.g. mean, median, standard deviation, coefficient of variation, etc.) can be calculated for each sample, allowing users to characterize heterogeneity of the surface sample (Fig. 4). Although samples are partially homogenized by mixing with a spatula after centrifugation and prior to analysis, multiple measurements provide an

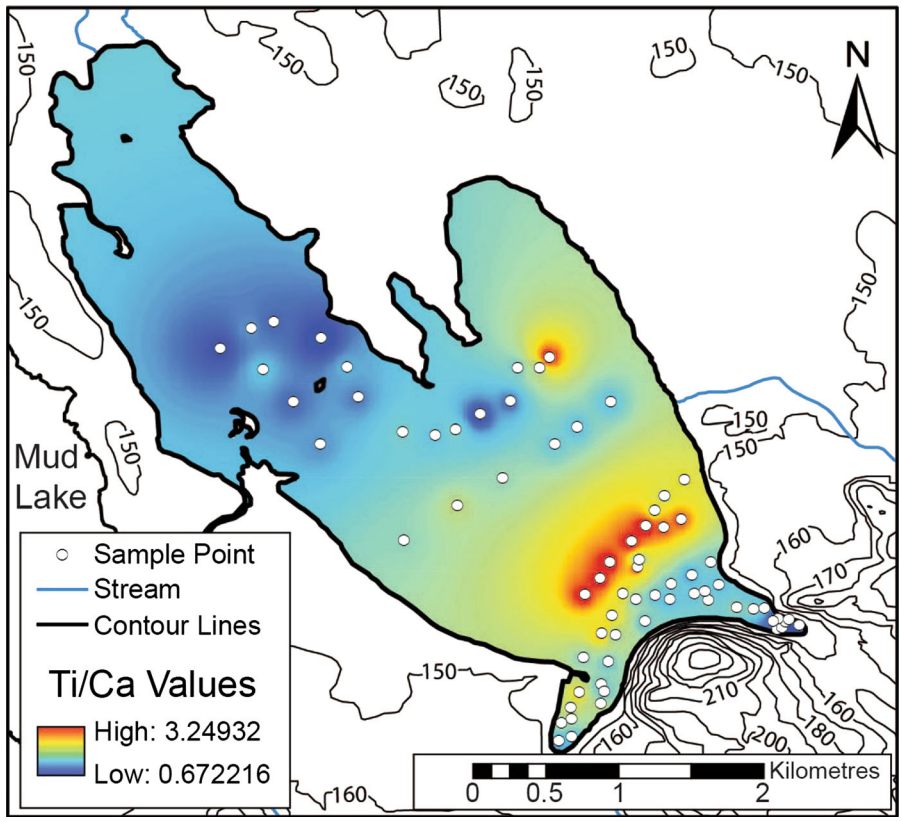


Fig. 5 Ti/Ca values for Harvey Lake, NB, Canada. Seventy-one surface samples were analyzed using the Itrax-XRF at McMaster University. Values were interpolated using the IDW tool in ArcGIS. *Warm colors* represent higher Ti/Ca values, which indicate proportionally higher allochthonous sediment input. (Color figure online)

opportunity to assess intra-sample variation that would be prohibitively expensive with other analytical techniques, and thus offer an advantage over techniques that assume a single measurement is representative of the analyzed sample (ICP-MS, benchtop XRF, WD-XRF).

Application of the SSR

In summer 2015, 71 sediment–water interface samples were taken from Harvey Lake, York County, New Brunswick, Canada (N45.745°, W67.03°), and analyzed using the SSR at the Itrax-XRF core-scanning facility at McMaster University, Hamilton, Ontario. Samples were analyzed at 0.2-mm resolution for 15 s/point at 15 mA and 30 kV, using a Mo-anode x-ray tube in three separate runs. Geological Survey of Canada Stream Sediment Standard 3 (STSD-3) was rehydrated from powdered form, using de-ionized water to achieve a consistency similar to surface sediment samples, and was loaded in SSR compartments at the start and end of each run of Harvey Lake samples. Preparing samples and loading them into the SSR took ~6 h of active time. Analysis with the Itrax-XRF took ~25 h and generated >3000 data points after post-processing. Density plots for replicate analysis of STSD-3 show good agreement between peaks, suggesting good reproducibility between scans, i.e. within expected variations caused by changes in bulk density and water content that may have occurred during rehydration and subsequent drying during analysis (Fig. 4). Density plots also show near normal distribution, implying that mixing samples with a spatula adequately homogenizes the sediment. Reducing the scan resolution would significantly reduce the required scan time, and based on the results obtained for Harvey Lake, would yield a similar outcome. Figure 5 shows Ti values normalized to Ca. Values between sample points were interpolated using inverse distance weighting (IDW). Ti/Ca is a proxy for relative change in allochthonous input as variations in Ti can be caused by changes weathering or sediment transport within a given catchment area

(Davies et al. 2015). High Ti/Ca values, however, may be a result of variations in Ca content caused by productivity changes across the lake basin. Elevated Ti/Ca values occur in the southern basin where a nearby stream and steep hill result in high deposition rates. This may be an ideal site for future paleoenvironmental studies using conventional sediment cores.

Conclusions

The SSR enables researchers to carry out inexpensive geochemical studies through analysis of discrete sediment samples using the Itrax-XRF core scanner. The use of this durable, easy-to-assemble sample vessel can maximize the spatial resolution of analyzed sediment samples in between- and within-lake studies that seek to characterize the range of lake environmental variability, and allow for more direct comparisons with conventional core analyses that employ the Itrax.

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