APPENDIX C. CHARACTERIZATION OF AMPHIBOLE FIBERS FROM ORE ORIGINATING FROM LIBBY, MT; LOUISA COUNTY, VA; AND PALABORA, REPUBLIC OF SOUTH AFRICA

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The O.M. Scott plant in Marysville, OH manufactured a number of products including fertilizers, dyes, and pesticides that were bound to a vermiculite carrier as a delivery vehicle. The plant received ore from Enoree, SC; Louisa County, VA; Libby, MT; and Palabora, Republic of South Africa, which was processed in an exfoliation furnace to produce vermiculite used in the manufacture of their commercial products. Only ore from South Carolina was used in 1957 and 1958. From 1959 to 1971, ores from South Carolina and Libby, MT were used. From 1972 to 1980, ores from Libby, MT, South Africa, and Virginia were used. No ore from Libby, MT was used after 1980. Only ore from South Africa and Virginia was used after 1980 (see Appendix F).

The U.S. Environmental Protection Agency (EPA) Region 8 obtained samples of ore from Libby, MT, South Africa, and Virginia from Dr. James Lockey, University of Cincinnati, and analyzed the samples to determine mineralogy and particle size distribution (length, width, and aspect ratio) using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) to identify the nature of the amphibole fibers. Dr. Lockey obtained the South African and Virginia ore samples from the Marysville, OH facility in 1980 and the Libby, MT ore (Libby #3 ore) from an expansion plant in Salt Lake City, UT, in 1981. Region 8 was unable to obtain vermiculite or ore from the Enoree, SC mine complex.

The ore from the Rainey Creek complex (Vermiculite Mountain Mine, Libby, MT) resides in large ultramafic intrusive bodies that are rich in biotite, pyroxenite, and biotitite, a rock comprised of almost pure biotite. The ultramafic intrusions are cut by deposits of syenite and carbonatite, and much of the biotite has been hydrothermally altered to hydrobiotite and vermiculite (Meeker et al., 2003; Frank and Edmund, 2001). The pyroxenite has been altered to fibrous soda-rich amphiboles, and contacts with pyroxenite surrounding the biotitite contain the vermiculite ore zone containing diopside, hydrobiotite, and apatite. Fibrous and nonfibrous amphiboles are located in both veins and disseminated throughout the intrusive rock along cleavage planes of pyroxene. Amphiboles from Vermiculite Mountain had been referred to as soda tremolite, richterite, soda-rich tremolite, tremolite asbestos, and richterite asbestos by a number of investigators. In 2000, Wylie and Verkouteren (2000) identified winchite as the principal amphibole in the Vermiculite Mountain deposit based on chemical investigation referencing the classification system of Leake et al. (1997) and optical properties. Meeker et al. (2003) investigated amphibole types from the mine complex using electron probe microanalysis

and X-ray diffraction analysis and reported the presence of winchite, richterite, tremolite, and magnesioriebeckite. Magnesio-arfvedsonite and edenite were detected in low abundance. The amphibole composition of the Libby Amphiboles is roughly winchite, richterite, tremolite, magnesio-riebeckite, magnesio-arfvedsonite, and edenite (84:11:6:<1:<1:<1). The O.M. Scott facility received ore from the Vermiculite Mountain mine complex, Libby, MT from 1959 through 1980.

The Palabora Igneous Complex, located near Phalaborwa, Republic of South Africa, is the location of the Palabora mine. The Palabora ore deposit shares many features with the Vermiculite Mountain mine complex—including zoned deposits with ultramafic rocks (pyroxenite) and intrusion by alkalic rock, primarily syenite. The primary mica at Palabora is phlogopite rather than biotite, and the primary alteration product that forms vermiculite ore is hydrophlogopite rather than hydrobiotite (Schoeman, 1989).

The Palabora ore is reported to contain little or no asbestiform fibers based on polarized light microscopy by the Institute of Occupational Medicine in Edinburgh (IOM Consulting, 2008). Crude vermiculite from the Palabora complex was also reported to be free of asbestiform fibers by polarized light microscopy (IOM Consulting, 2008). In both reports, the analysis by polarized light microscopy was conducted with a detection limit of 1 ppm, and, since no chrysotile or amphibole structures were detected, no further analysis by electron microscopy and X-ray diffraction were conducted.

The ore from the Virginia Vermiculite mine in Louisa County, VA is described as mafic rock intruded by a series of small pegmatites (Gooch, 1957). Meisinger (1979) classified the deposits as Type 3, similar to the ores from Enoree, SC. The formations consist of potassic ultramafic bodies, primarily biotite. The vermiculite ores are found primarily in hydrobiotite portions of the biotite intrusions. The hydrobiotite deposits are preferentially mined because of better commercial properties compared to vermiculite.

There is limited information on the asbestos content of the ores from the Louisa County deposit. Rohl and Langer (1977) reported both chrysotile and amphibole fibers in six ore samples from the Louisa County deposit. The chrysotile was reported as fibers and bundles while the amphiboles fibers were classified as actinolite. Moatamed et al. (1986) analyzed a Virginia ore sample collected at a processing plant in Salt Lake City, UT and reported traces of fibrous amphibole asbestos identified as actionlite in the form of cleavage fragments having low

aspect ratios. Amphibole content for both unexfoliated and exfoliated ores ranged up to 1.3% amphibole asbestos.

Ores from the Enoree, SC deposits are primarily hydrobiotite and biotite in origin. Fluroapatite is a common mineral collocated with the hydrobiotite. Zircon is also widely dispersed throughout the plutons along with minor accessory minerals including talc, chlorite, chromite, rutile, titanite, corundum, anatase, and amphibole asbestos (Hunter, 1950). The amphibole asbestos identified in the vermiculite deposit at Enoree, SC has been classified as tremolite (Libby, 1975).

As previously noted, EPA Region 8 obtained samples of ore from Libby, MT, South Africa, and Virginia from Dr. James Lockey, University of Cincinnati, and analyzed the samples to determine the particle-size distribution (length, width, and aspect ratio), using TEM and EDS to identify the mineral composition of the amphibole fibers. Region 8 was unable to acquire a sample of ore from the South Carolina Enoree mine complex for analysis. Region 8 conducted analysis of the ore and exfoliated materials to connect the exposures of workers to mineral fibers in Marysville, OH, to the ore originating in Libby, MT. The connection is based on fiber morphology, mineralogy, and fiber-size similarities.

In order to analyze the fibers from the ore and vermiculite bulk material, the fibers must be loaded onto filters and prepared for analysis by TEM. Three potential methods were considered for transferring the fibers from the bulk material to filters: water elutriation, glove-box transfer, and the fluidized bed asbestos segregator (FBAS). Of these three methods, only the glove-box and FBAS involved physical disturbance of the bulk material to elutriate fibers into the air that might be similar to handling and processing of ore in the Marysville, OH plant. Due to the limited quantity of test material available for analysis, Region 8 employed the FBAS as an analytical instrument to load the mineral fibers onto filters for TEM analysis.

Briefly, samples of ore and vermiculite were prepared following the procedure outlined by Bern et al. (2002). Samples were dried, ground with a Wylie mill and mortar and pestle, and sieved through a 230-μm (60 mesh) sieve. Samples (exactly 2.0 g) were mixed with 18 g of analytical silica sand and placed in a FBAS vessel to load 25-mm mixed cellulose ester air sampling filters (0.8-μ pore size). The FBAS was run for 3 minutes to load the filter cassettes with sufficient fibers for analysis by TEM. Five filters were loaded for each of the ore and

vermiculite samples. After loading, the filters were prepared for TEM analysis by mounting on copper grids, carbon coating, and subjected to TEM analysis (TEM-ISO 10312 method).

The laboratory followed fiber counting rules detailed in the Quality Assurance Project Plan for the specific study using Libby-specific laboratory modifications. Total amphibole fibers and Phase Contrast Microscopy equivalent (PCMe) fibers were counted for each of the ore/vermiculite samples as described in Appendix B. A total of 1.0 mm^2 area or a total of 200 asbestos structures were counted to achieve the desired analytical sensitivity (1/g; 1.5×10^4). DS was performed on selected samples from each of the vermiculite/ore samples to provide mineral characterization of individual fibers. Fiber counts were recorded on National Asbestos Data Evaluation Sheet data sheets for further analysis. Only the Libby, MT vermiculite and Libby, MT ore samples had sufficient fibers detected to construct a fiber-size distribution.

Fiber counts were determined by counting fiber numbers for a specific area of the filter grid or a specific number of grid openings (whichever was achieved first) to determine total fibers present. As shown in Table C-1, the number of fibers for the test materials varied greatly depending on the source, and the grid area measurement was exceeded prior to the fiber count metric (167 grid openings ~1.0 mm^2).

Table C-1. Fiber detected in ore and expanded product

Sample type	Grid openings	Structures counted			Concentration (s/g)		
		LA	OA	C	LA	OA	C
Virginia Ore	167	0	0	0	0	0	0
Virginia Expanded	167	1	0	0	13,008	0	0
South Africa Ore	167	2	0	2	26,403	0	26,403
South Africa Expanded	167	0	0	0	0	0	0
Libby #3 Ore	167	320	0	0	1,393,873	0	0
Libby Expanded	167	100	0	0	468,213	0	0

LA = Libby Amphibole, OA = Other amphibole, C = Chrysotile. Note: the designation of fibers as Libby Amphibole in this instance reflects only a qualitative morphological comparison to amphiboles of the Libby, MT series.

The Libby #3 ore and the Libby #3 expanded material contained the greatest number of fibers both in fiber counts on the filters and in calculated structures per gram of bulk material.

Virginia expanded and South African ore contain amphibole structures represented by low fiber counts. South African ore also contained chrysotile fibers as determined by morphology and EDS analysis. The absence of fibers detected in the Virginia ore and the South African-expanded materials probably represents actual low fiber content of the ore and is a function of the detection limit for the structure analysis. The estimation of structures per gram of material indicated that there were 13,000 to 26,000 fibers per gram of bulk material, which was approximately 18 times lower than the Libby, MT ore samples. The decrease in fibers found in the Marysville, OH facility after 1980 when only ore from Virginia, Palabora, and South Carolina was used (see Appendix F) is consistent with the findings of low fiber counts for the Virginia and Palabora materials. In addition, numerous nonasbestiform minerals were also detected including biotite, micas, and pyroxenes in the bulk materials from Virginia and South Africa.

Amphiboles are a complex group of minerals characterized by double chains of silicate tetrahedrons and the generic chemical formula of $A_{0-1}B_2C_5T_8O_{22}[OH]_2$ where A, B, C, and T represent the various cations. The modern classification system of amphiboles is described in Leake et al. (1997). To classify the mineral species of the amphibole, it is not sufficient to determine its composition; the various cations must be assigned to the specific A, B, C, and T sites. The cutoffs of the compositional ranges allowed for each amphibole mineral species are based on the number of the cations in the various sites. The methodology to classify an amphibole is to first determine its elemental compositions (e.g., as expressed as weight percent oxide for each element or as atomic percent for each element). Then a normalized routine is applied to the raw elemental measurements to calculate the number of each of the cations contained in one formula unit. (This is a simple arithmetic calculation since the cation percents have been measured, and the stoichiometry must balance the charges of the cations and anions.) Generally, one formula unit is assumed to contain 23 oxygens. Next, the sites are filled up by assigning cations to them subsequently, specifically:

T: Si^{4+}, Al^{3+}, and Ti^{4+}.

C: Al^{3+} and Ti^{4+} (only after the *T* sites are filled first) and then Mg^{2+}, Fe^{2+}, Fe^{3+}, and then Mn^{2+}.

B: Any remaining Mg^{2+}, Fe^{2+}, and Mn^{2+} (after the *C* sites are filled), all Ca^{2+}, then Na^{+} if there is any room left.

A: Na^{+} and K^{+} only.

Once the cations are assigned to their sites, it is a simple matter to classify the minerals based on the cutoffs of the composition field allowed for each mineral.

The Libby Amphibole asbestos[1] group of minerals is a complex group of amphiboles consisting of six minerals:

- Winchite, $CaNa[Mg, Fe^{2+}]_4[Al, Fe^{3+}]Si_8O_{22}[OH]_2$
- Richterite, $NaCaNa[Mg, Fe^{2+}, Mn, Fe^{3+}]_5Si_8O_{22}[OH]_2$
- Tremolite, $Ca_2Mg_5Si_8O_{22}[OH]_2$
- Magnesio-riebeckite, $Na_2[Mg_3, Fe^{3+}_2]Si_8O_{22}[OH]_2$
- Magnesio-arfvedsonite, $NaNa_2[Mg_4,Fe^{3+}]Si_8O_{22}[OH]_2$
- Edenite, $NaCa_2Mg_5Si_7AlO_{22}[OH]_2$

Libby Amphibole is characterized by a low amount of Al in the *T* site—and a correspondingly high Si content—so, according to Leake's (1997) classification, if the Si (expressed as atoms per formula unit, apfu) is at least 7.5, and Al content in the *T* site is <0.5, all 6 Libby Amphibole types can be plotted on a graph of Na content of the *B* site versus the (Na + K) content in the *A* site. This approach was described by Meeker et al. (2003) for the Rainy Creek complex.

EDS spectra (TEM/EDS) were collected from all amphibole fibers found in the South Africa and Virginia samples, and six randomly selected Libby Amphibole asbestos fibers in each

[1]The term "Libby Amphibole asbestos" is used in this document to identify the mixture of amphibole mineral fibers of varying elemental composition (e.g., winchite, richterite, tremolite, etc.), that have been identified in the Rainy Creek complex near Libby, MT. It is further described in Section 2.2.

of the Libby, MT ore and Libby, MT expanded samples. Two bundles of asbestiform serpentine (chrysotile) were found in the South African ore sample. EDS spectra were collected for one of the bundles. The chemical formula of serpentine is $Mg_3Si_2O_5[OH]_4$. The EDS software package collected and summarized each spectrum to determine the atomic percent of each element of interest.

Several assumptions were made in the treatment of the TEM/EDS data:

1. Numbers of cations per formula unit are calculated on the basis of 23 oxygens. This may or may not be correct because an [OH] site in the amphibole crystal can be occupied by either OH^-, F^-, Cl^-, or O^{2-}. The calculated cation numbers will be affected if a significant quantity of O^{2-} is in the OH site.

2. A persistent problem with amphiboles is that they can contain both ferric [3+] and ferrous [2+] iron in the same crystal. For the purposes of this report all Fe was assumed to be Fe^{2+}. A method for calculating the ratio of Fe^{2+} to Fe^{3+} is described in Leake et al. (1997), but it is very complex, applies to polished sections, and was not attempted for this report.

3. For the purposes of this report, the *T* sites were assumed to be filled completely full to 8 apfu, and the *C* sites were assumed to be completely full to 5 apfu. All Ca and any Mg, Fe, and Mn remaining after the *C* site was full were then assigned to the *B* site. Next, Na was assigned to the *B* site until it was full (2 apfu), then any remaining Na and all K were assigned to the *A* site.

Applying these assumptions to the TEM/EDS data produces a useable graph of the Na and K content of the amphibole fibers. As shown in Figure C-1, Libby #3 ore and Libby #3 Expanded amphiboles were characteristic of winchite and tremolite. Virginia Expanded and South African ore both contained amphibole fibers characteristic of non-Libby (Na and K) in the tremolite series.

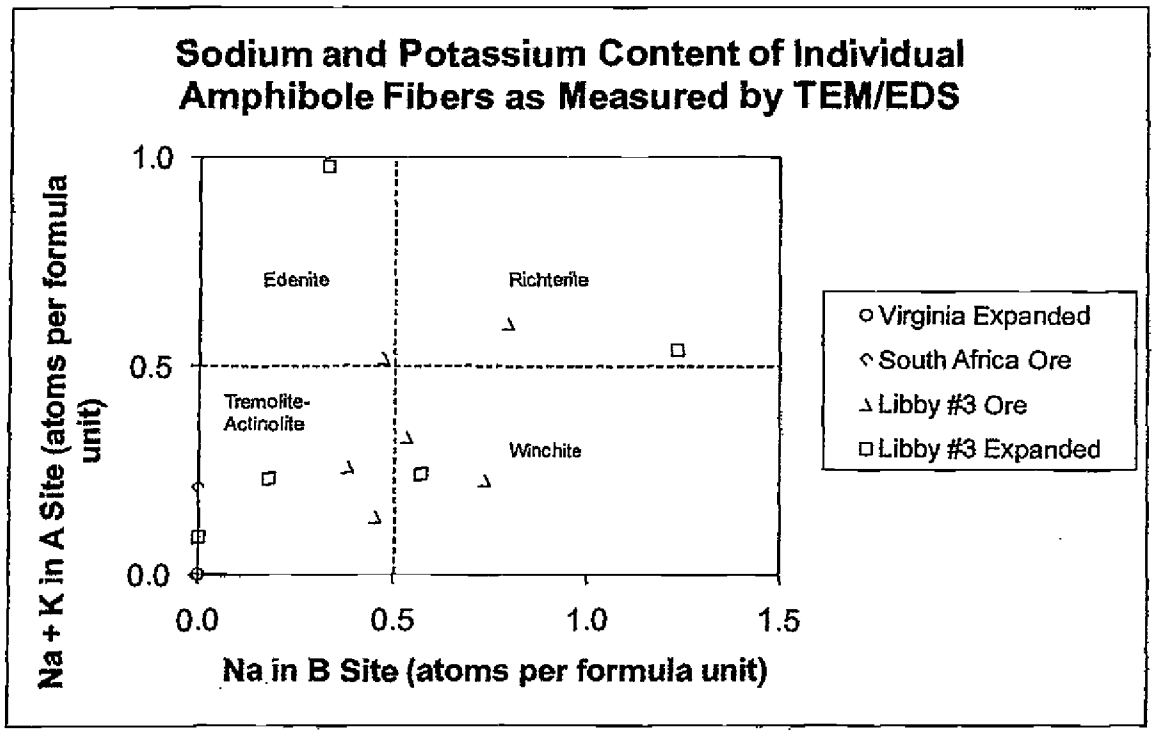

Figure C-1. Cation values for Na in the *B* site and the Na + K in the *A* site from individual amphibole fibers.

Following all assumptions described above and the approach of plotting Na in the *B* site versus Na + K in the *A* site as described by Meeker et al. (2003), the mineral species of the Marysville, OH fibers can be described as:

- The single Virginia amphibole asbestos fiber is an actinolite
- Both of the South African amphibole fibers are tremolite
- 8 of the Libby Amphibole asbestos fibers from Libby, MT are winchite
- 4 of the Libby Amphibole asbestos fibers from Libby, MT are tremolite

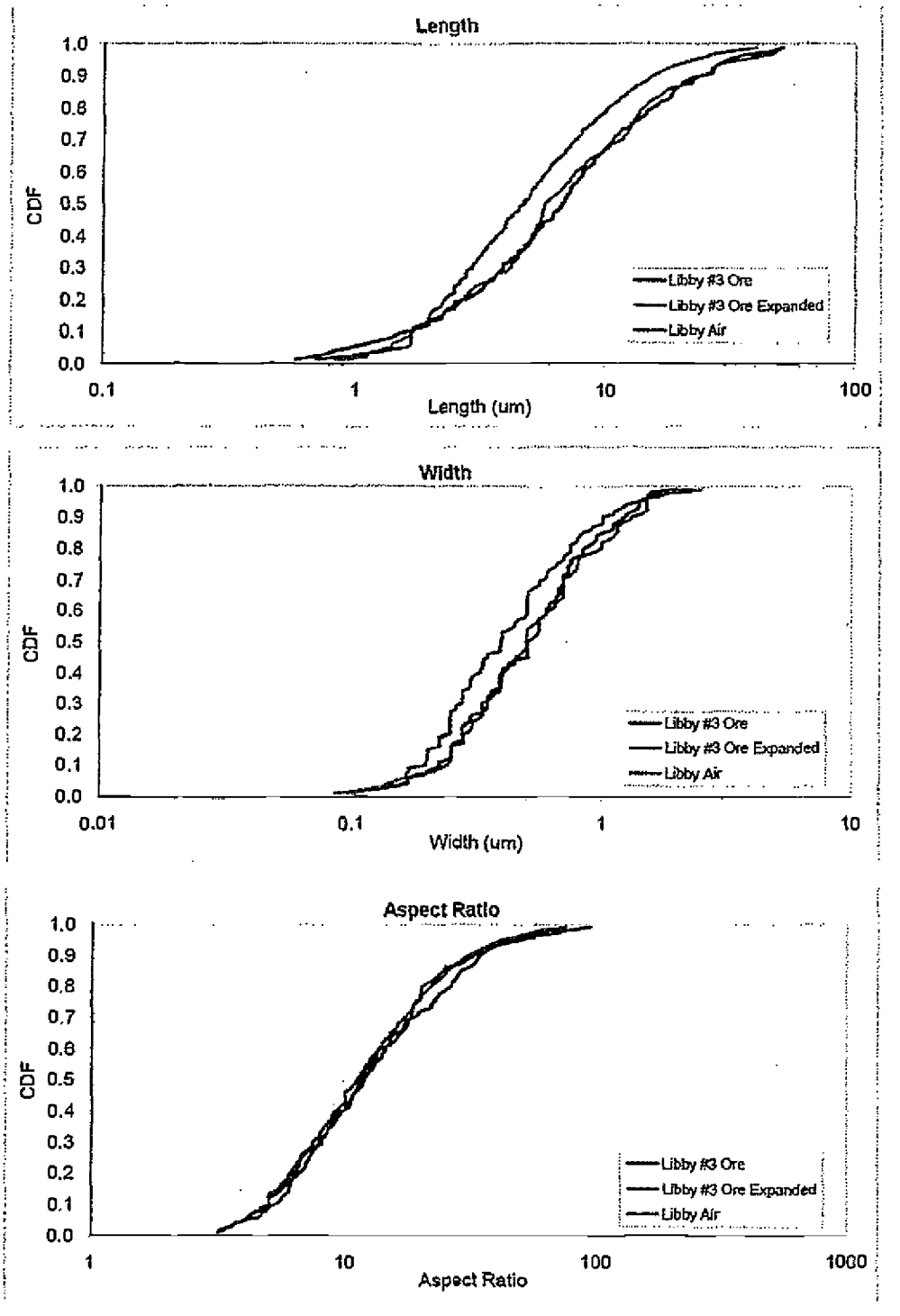

Figure C-2. Fiber-size distribution of Libby Amphibole asbestos.

Fiber-size distributions for amphibole fibers from the Libby #3 ore and Libby #3 expanded sources were conducted on the fibers counted during the TEM analysis of the filter grids. Due to the low fiber count detected in the Virginia and South Africa sources, it was not possible to develop a fiber-size distribution for these fibers. The Libby Amphibole asbestos fiber-size data were plotted as a cumulative distribution frequency for fiber length, fiber width, and aspect ratio. These data were compared to Libby Amphibole asbestos fibers collected in Libby, MT as part of EPA's ongoing ambient air monitoring program and the Libby Asbestos Superfund site (see Appendix B). The Libby, MT ore and expanded material showed an increased frequency of longer and wider fibers than the fibers from the Libby, MT ambient air-sampling program. Aspect ratios were nearly identical. The differences between the length and width frequency were not outside of the expected range for Libby Amphibole asbestos fibers and were consistent with fiber-size distributions for soil activity-based-sampling data from Libby, MT.

Based on the TEM morphological analysis of filter grids, TEM/EDS analysis for the fiber mineralogy, and the fiber-size distribution data, it can be concluded that the amphibole fibers detected in the Libby # 3 ore samples from the Salt Lake Expansion facility are consistent with data from authentic Libby Amphibole fibers (Meeker et al., 2003) found in Libby, MT (see also Appendix B). Further, ore samples from Virginia and South Africa contained amphibole and chrysotile fibers but at a much lower frequency of detection than the Libby Amphibole ore as reported in Appendix F.

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