Preparation and Characterization of "Libby Amphibole" Toxicological Testing Material

Open-File Report 2012–1012

U.S. Department of the Interior
U.S. Geological Survey

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KEN SALAZAR, Secretary

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Introduction

The U.S. Environmental Protection Agency (USEPA) began work in Libby, Mont. in 1999 when an Emergency Response Team was sent to investigate local concern and media reports regarding asbestos-contaminated vermiculite. Since that time, the site has been granted Superfund status and site remediation to a safe level of asbestos has been ongoing. The amphibole asbestos from the Vermiculite Mountain vermiculite deposit near Libby, Mont. (Libby amphibole) is unusual in the sense that it is currently not classified as one of the regulated six asbestos minerals—chrysotile (a serpentine mineral) and the amphibole minerals amosite (asbestiform cummingtonite-grunerite), crocidolite (asbestiform riebeckite), asbestiform anthophyllite, asbestiform tremolite, and asbestiform actinolite. The amphiboles from the Vermiculite Mountain vermiculite deposit, primarily winchite and richterite, are related to tremolite and in the past have been referred to as sodium-rich tremolite or soda tremolite (Larsen, 1942; Boettcher, 1966; Wylie and Verkouteren, 2000; Gunter and others, 2003; Meeker and others, 2003). The public health issues in Libby, Mont. have brought to light many of the inconsistencies in the literature regarding fiber characteristics, nomenclature, and toxicology.

To better understand the toxicological characteristics of the Libby amphibole, investigators require a sufficient quantity of material representing the range of fibrous amphiboles present in the vicinity of Vermiculite Mountain to use in toxicology studies. The material collected in 2000 (Meeker and others, 2003) has been exhausted and a second collection and preparation effort, funded by the USEPA, was conducted in 2007. Both the 2000 (LA2000) and 2007 (LA2007) materials were generated to support research needs identified by the USEPA and the National Toxicology Program, and new in-vivo and in-vitro toxicology studies are underway. This Open-File Report describes the process of preparation and summarizes the chemistry and mineralogy of the LA2007 toxicological testing material.

Sample Collection

Thirty samples were collected from the Vermiculite Mountain mine site and described by Meeker and others (2003). Of those 30 samples, 6 were mixed to produce the LA2000 (also called the "six-mix") sample that has been characterized (Bellamy and Gunter, 2008) and used in several toxicology-related studies (Blake and others, 2007, 2008; Duncan and others, 2010; Heintz and others, 2010; Hillegass and others, 2010; and Smartt and others 2010). The six samples used for the LA2000 material correspond to samples 20, 23, 25, 27, 28, and 30 as identified in Meeker and others (2003). These six samples were combined to approximate the compositional space of the amphibole minerals from the mine (see figures 6 and 7 in Meeker and others, 2003). In addition,

the LA2000 material was ground to approximate the length, width, and aspect ratio of fibers reported for the Libby air data (fig. 1) (compare U.S. Environmental Protection Agency, 2010).

Since the supply of LA2000 has been exhausted, the need to "recreate" this sample prompted two sampling trips to the Vermiculite Mountain mine in May and September of 2007 (fig. 2). Where possible, the same sites sampled in 2000 were re-sampled. One of the sites sampled in 2000, sample 28, was inaccessible in 2007 due to slope failure. The first trip in May 2007 was a reconnaissance trip to collect small samples for analysis in order to determine the best sample site locations to approximate the LA2000 sampling material based on amphibole chemistry, mineralogy, morphology, and minimizing accessory phases. The eight samples collected in May were returned to the USGS analytical laboratories and analyzed by electron microprobe and x-ray diffraction.

Based on analytical results from the May reconnaissance trip, approximately 300 kilograms (kg) of amphibole-rich rock was collected at the Libby mine in September of 2007. Samples were collected by removing amphibole-rich rock from veins in cut faces and from large boulders in previously mined areas of the property. Amphibole-rich rock was removed using stainless steel chisels either by hand or with chipping hammers and returned to a base camp set up on the mine property (fig. 3A). At the base camp (fig. 3B), larger pieces of material were placed on a large plastic sheet and further reduced in size using chisels and sledge hammers (fig. 3C). The most amphibole-rich material was then placed in a large steel shatter box and reduced to gravel-size pieces or smaller using a sledge hammer. During this process, pieces of rock that contained significant visible amounts of contaminants such as pyroxene, biotite, and vermiculite were removed.

After reducing the sample material to gravel-size or less, the material was sieved and put through a jaw crusher to reduce the material to millimeter-size or less (fig. 3D). Representative aliquots of the reduced material for each sample were removed and placed in plastic zip-lock bags for analysis by X-ray diffraction (XRD), electron probe microanalysis (EPMA), scanning electron microscope-energy dispersive spectroscopy (SEM/EDS), and inductively coupled plasma mass spectrometry (ICP-MS) at the USGS laboratories in Denver, Colo. The reduced material from individual sample sites was then placed in double plastic bags, weighed, and sealed into 5-gallon (gal) pails for shipment. Of the eight samples returned, a mixture of three was chosen to best approximate the chemical and morphological variation of the LA2000 material (see analyses below). Table 1 lists the coordinates of the three samples chosen for the LA2007 material.

Preparation of the LA2007 Material

Based on EPMA and XRD analyses of the May 2007 reconnaissance samples and representative aliquots of the September 2007 samples referred to in the preceding section, three individual samples were chosen to comprise the mixture. The individual samples 070917-1, 070918-5, and 070920-2 were chosen to prepare the 2007 Libby amphibole material because they contain the least contaminants (table 2) and provided a similar distribution of data points in the compositional space reported by Meeker and others 2003 (fig. 4) (see following data). The weight percentages of each sample were determined to provide the best match possible to the overall chemistry and mineralogy of the amphibole in the mine and the composition of the LA2000 sample. It was determined that LA20007 should be mixed in the following proportions: 90 percent by weight of sample 070918-5 (primarily winchite) and 5 percent by weight each of samples 070917-1 (primarily tremolite) and 070920-2 (primarily richterite and winchite). The goal was to produce approximately 10 kg of the composite amphibole material.

The individual samples from the 5-gal buckets packaged in Libby (described above) were processed at the U.S. Geological Survey (USGS) facilities in Lakewood, Colo., in a negative-pressure room specifically designed for working with asbestiform minerals. Approximately two liters of crushed, reduced material and three liters of deionized water were transferred to a 1-gal stainless steel, four-speed Waring commercial blender (model 31BL79). The mixture was processed for approximately 2 minutes (min) at the lowest speed. The blended slurry was then quantitatively transferred to a five gallon container lined with a plastic bag. This procedure was repeated until the correct amount of each specific amphibole needed for the final material was processed.

Aliquots of this "chopped" material were then ground using a 10-liter (L) ceramic ball jar filled with ¾-inch (in) alumina grinding cylinders and a customized USGS horizontal roller mill (fig. 5). In this procedure, approximately 2 L of "chopped" material were transferred to the ball jar along with 3 L of deionized water. The jar was sealed, its outside surfaces wiped clean and the jar transferred to the horizontal roller mill located adjacent to the hood. The roller mill was operated at approximately 20 rotations per minute for a period of 6 hours (hr). The duration of the grinding period was controlled using a commercial timer.

After the grinding period, the ball jar was transferred back to the asbestos hood. The asbestos suspension was separated from the grinding media and transferred to a 5-gal container lined with a plastic bag. The alumina grinding cylinders were rinsed and the rinse solution was transferred to the 5-gal asbestos container. The grinding cylinders were then transferred back to the ball jar along with a second aliquot of "chopped" amphibole and a new supply of deionized water. After the second round of grinding, the liquid used in grinding was switched from deionized water to the supernatant solution from the ground asbestos container following a 6-hr settling period. This recycled water was clear and contained no obvious signs of suspended amphibole material. The supernatant was removed from the 5-gal asbestos container using a siphon process which minimized any disturbance of the ground amphibole material during removal. Use of this recycled water helped minimize the amount of contaminated water that would require processing during later stages of material preparation.

For each individual sample, after grinding was completed, the container of processed material was allowed to evaporate to dryness. After the samples reached apparent dryness, the container was sealed, its outside surfaces wiped clean with paper towels, and the container was transferred to a plastic trash bag which was then sealed. The bag containing the asbestos samples were removed from the hood and weighed to obtain an estimate of the sample mass. Prior to the final blending stage, a percent moisture determination was performed on the three individual processed asbestos types. The percent moisture value was determined by taking 5 aliquots of each asbestos sample using a sample thief and combining the aliquots in a pre-weighed glass bottle. Bottle weights before and after drying (110°C) were obtained in order to estimate the percent moisture content of each container. To achieve the desired blending ratio of the three asbestos samples, a calculated amount of each sample, taking into account water content, was combined in an unlined 5-gal container. Deionized water was added to the 5-gal container to obtain a fluid suspension that was easily mixed. All blending was performed using a cordless drill equipped with a standard commercial paint mixer. Blending typically lasted for a period of 10 min at low to moderate drill speed. A total of three batches of blended material was prepared in this manner. To ensure the consistency of the final material, aliquots of each batch were transferred in a random manner between the other containers and then briefly mixed.

In the final preparation step, aliquots from each container were randomly transferred to a 4-in x 9-in x 16-in stainless steel drying pan on a standard laboratory hot plate. The hot plate was fitted with an aluminum foil tent to prevent splatter, and the material was allowed to evaporate to dryness, usually overnight. After drying, the contents of the pan were lightly disaggregated and then transferred to a plastic lined 5-gal container. This process was repeated until the desired amount (roughly 10 kg) of blended material was obtained. A summary of the process is presented in figure 6.

Chemical and Mineralogical Analyses

Bulk Chemical Analysis

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP-MS were performed on the three individual samples that went into the LA2007 composite material as well as on two aliquots of the LA2007 composite material. ICP-MS was performed with a Perkin-Elmer Model 6000 ICP-MS following a four acid (nitric, perchloric, hydrofluoric, and hydrochloric) dilution of the material (Briggs and Meier, 1999). Refractory phases such as chromite, zircon, and rare earth element-bearing phases may not completely dissolve in the acid digestion. For this reason, the sample was decomposed at 450°C in a sodium peroxide sinter for ICP-AES-MS. Because a sodium peroxide sinter is used, sodium (Na) and silicon (Si) are not analyzed by ICP-AES-MS. Additional analytical methods were used to measure elements gold (Au), mercury (Hg), selenium (Se), and tellurium (Te); however, these elements were below the detection limit of the method. The procedures for all methods are described at http://minerals.cr.usgs.gov/projects/analytical_chem/references.html.

The results of the bulk methods are summarized in table 3 and figure 7. The results are for informational purposes only and do not represent certified values. Few elements vary between the LA2000 and LA2007 samples. The notable differences are higher strontium, phosphorus, copper, niobium, and molybdenum in the LA2000 sample. These differences are explained by the presence of various accessory minerals such as celestine ($SrSO_4$), fluorapatite (Ca_5PO_4F), chalcopyrite (CuFeS2), and in the LA2000 which were not observed in the individual samples that went into the LA2007.

X-ray Diffraction Analysis

For X-ray Diffraction, a 2-gram aliquot of the processed individual and composite samples was passed through a 60-mesh sieve and then side packed into a PANalytical sample holder for analysis. The samples were scanned using the following conditions:
PANalytical "X'Pert Pro – MPD X-ray Diffractometer
Theta/Theta geometry
Cu long-fine-focus X-ray tube (nickel (Ni) filtered)
"X'celerator" solid state "strip" detector
instrument conditions are 45 kV, 40 mA
15 millimeter beam mask
½° anti-scatter slit
¼° divergence slit

½° receiving anti-scatter slit
¼° receiving divergence slit
step size 0.0167 degrees in continuous scan mode
scan range of 5 to 65 (or 90) degrees two-theta
sample spinner on
scan rate was 1 degree per minute for a total scan time of 1 hr

Identification of mineral phases was made using Material Data Inc. (MDI) Jade (V 9.1) search-match software using the International Center for Diffraction Data (ICDD) "2009 PDF-4" and National Institute of Standards and Technology "FIZ/NIST Inorganic ICSD" databases. Semi-quantitative mineral estimates were calculated using MDI Whole Pattern Fit (WPF) software which simultaneously calculates a whole pattern fit and a Rietveld refinement of the minerals. Reference minerals are selected from the database, some of which are "structure" references that represent ideal crystals of the mineral, and other entries are real-world mineral specimens. Each of these cards contains a full crystallographic description of the mineral. A calculated model of the observed pattern is produced by non-linear, least-squares optimization. The calculations, performed by the software, involve the application of various parameters to improve the fit of the model to the observed data. Modeling parameters include background reduction, profile fitting, and lattice constants that iterate to minimize a residual error between the calculated x-ray diffraction pattern from the selected references in comparison to the measured scan of the sample. All data were normalized to 100 percent based on the identified minerals. A full description of the WPF algorithm is available from MDI (Materials Data Inc., 2011).

X-ray diffraction analysis measures the crystalline portion of the sample. This does not include any amorphous phases that may be present. The WPF software normalizes the data to 100 percent for all identified phases. The typical detection limit by X-ray diffraction is between 1 and 3 weight percent (wt %), depending on the crystallinity of the phase and interferences from overlapping lines from other phases. Thus, there may be trace phases present, but not identified and they are not included in the model. The phases identified and their estimated weight percentages are given in table 2. Also included in table 2 are phases observed in polished thin sections during electron probe microanalysis but not detected by XRD.

Electron Probe Microanalysis (EPMA)

Quantitative EPMA of polished thin sections was performed using a five-wavelength spectrometer (WDS), fully automated, JEOL 8900 scanning electron microprobe, at the USGS in Denver, Colo. Analytical conditions were: 15 kilovolt (kV) accelerating voltage, 20 nanoampere (nA) beam current (cup), point beam mode, and 20-second (sec) peak, and 10-sec background counting time. Calibration was performed using well-characterized silicate and oxide standards. Analytical precision for major and minor elements based on replicate analysis of standards was better than plus or minus 2 percent relative concentration for major and minor elements and equal to counting statistics for trace (less than 1 wt%) elements. Oxide weight percent values were converted to cations based on 23 oxygen equivalents using the recommendations of Leake and others (1997). The chemical analyses and calculated mineral formula are summarized in table 4 and figure 4. Multiple analyses were acquired on each sample. The quality of the data depended largely on the fibrosity of the material. More fibrous material yielded lower quality data; thus, fewer analyses are averaged for each sample.

Size Characterization

Given that researchers working with the LA2007 composite material will likely conduct their own analyses to characterize fiber size distributions, it was determined that a size characterization of the LA2007 material was unnecessary at this time. The LA2000 and LA2007 composite materials were provided to the USEPA laboratories in Research Triangle Park, N.C. for water elutriation following the methods in Webber and others (2008). The elutriation was performed to create a material for intratracheal installation and in vitro toxicology studies that would closely match a rat-respirable fiber size distribution. The method for particle counting the water-elutriated material is described in Lowers and Bern (2010). The water-elutriated LA2007 material contained 98 percent particles with an aspect ratio greater than or equal to 5, mean length of 4.99 plus or minus 4.53 μm and mean width of 0.28 plus or minus 0.19 μm, with upper and lower values of length and width being 0.52–27.30 μm and 0.07–1.15 μm, respectively, as determined using transmission electron microscopy (Shannahan and others, 2011).

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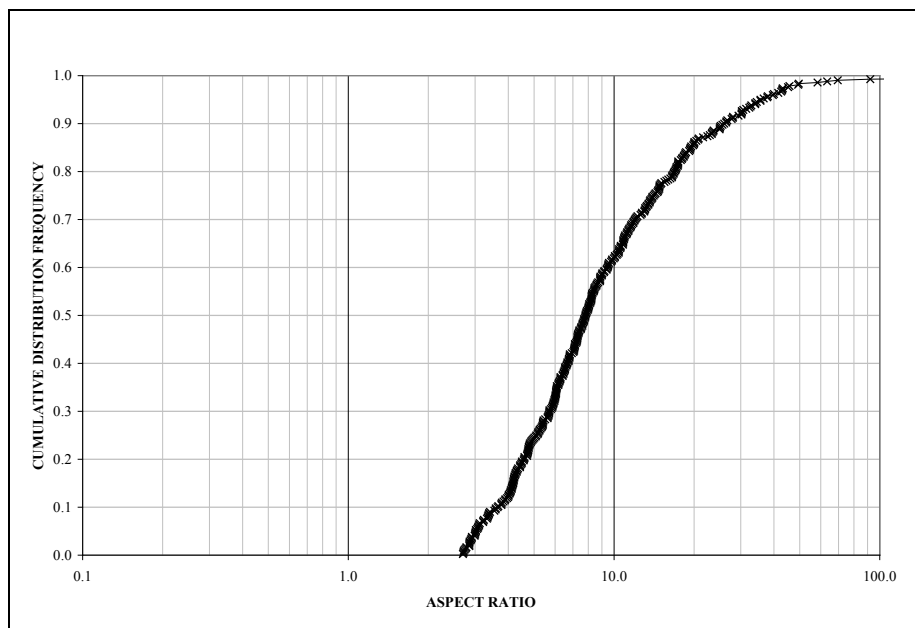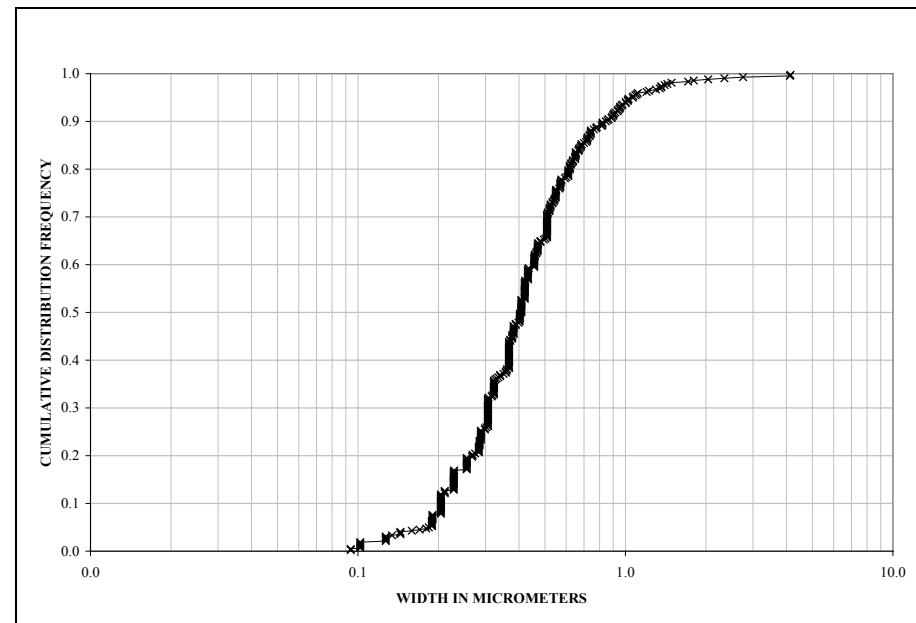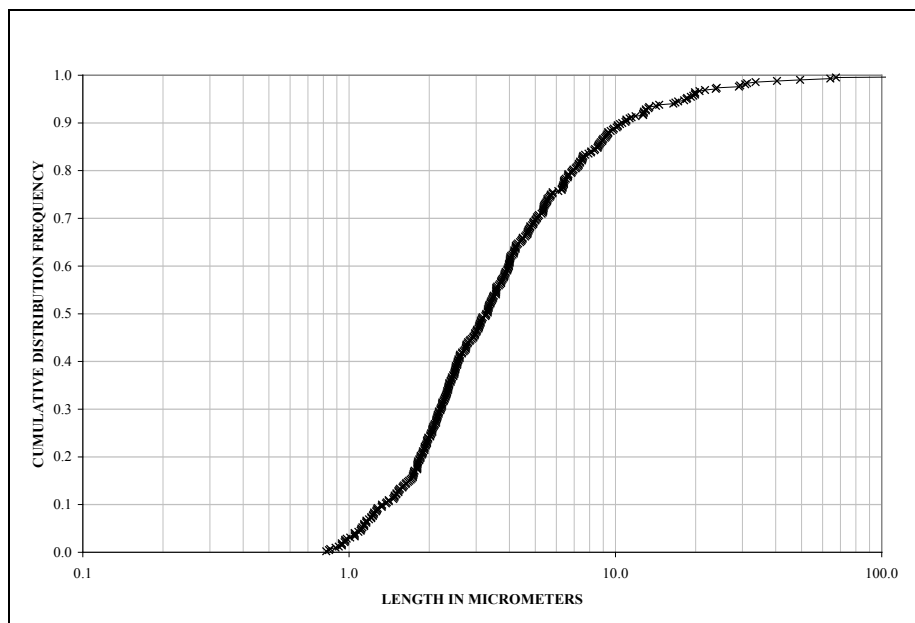
Figure 1. Cumulative frequency distribution of the length, width, and aspect ratio of Libby amphibole in the LA2000 mixture. Structures less than 0.8 micrometers (μm) in length and with aspect ratios less than 2.8 have been removed to better reflect the counting criteria for air sampling methods.
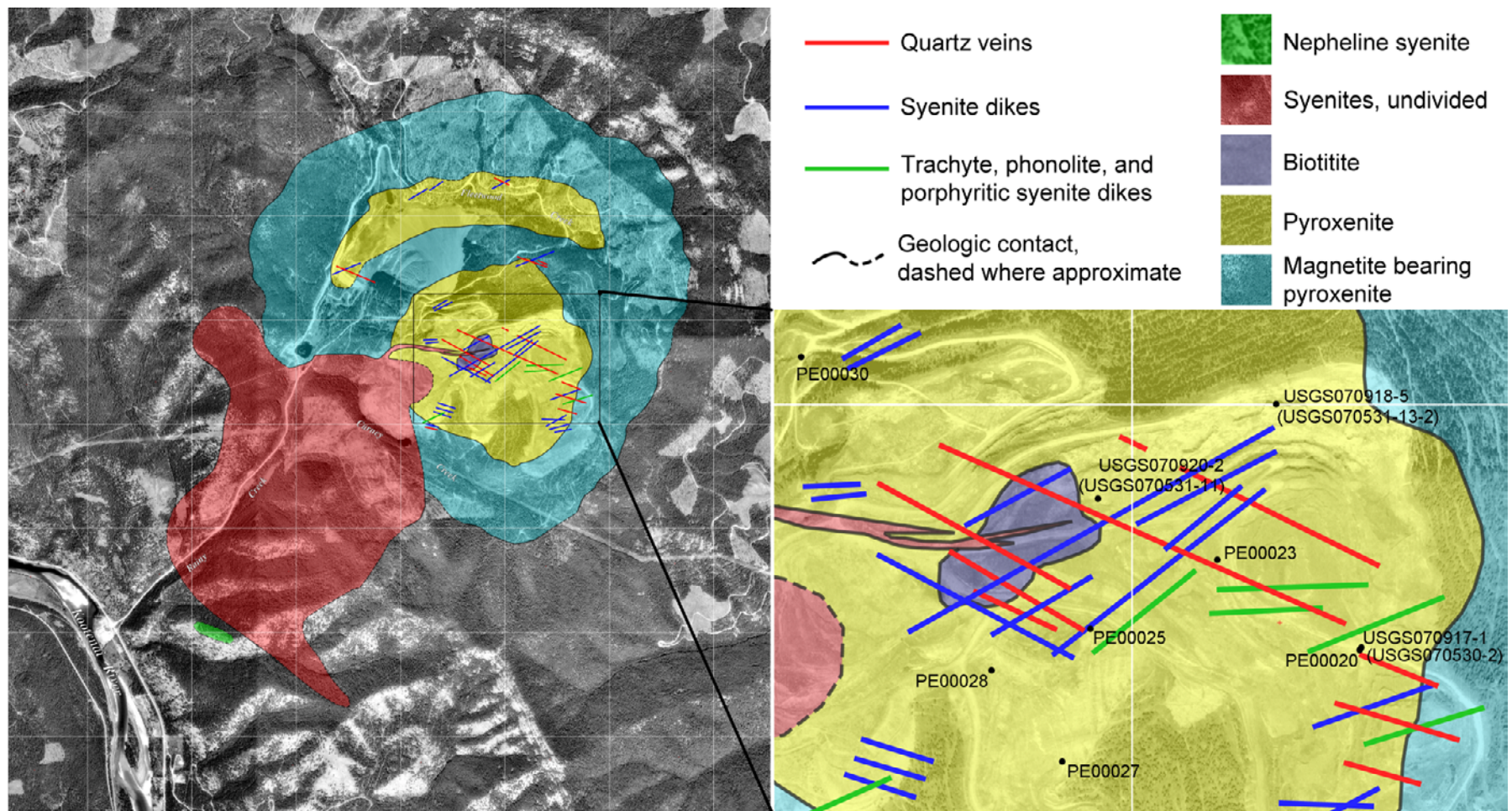
Figure 2. Generalized geologic map of the Vermiculite Mountain mine site. Sample locations from 2000 (PE) and 2007 (USGS) are shown. Only one of the locations sampled in 2000 was inaccessible during the 2007 sample collection.

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Figure 3. Sample collection process for the 2007 material. *A,* Removing material from an amphibole-rich vein. *B,* Base camp constructed near site USGS070918-5 to process samples prior to shipping. The base camp was built to contain the release of the fibers to the air during processing. *C,* Material was further reduced with sledge hammers and chisels until it was small enough to fit in the jaw crusher, *D.*
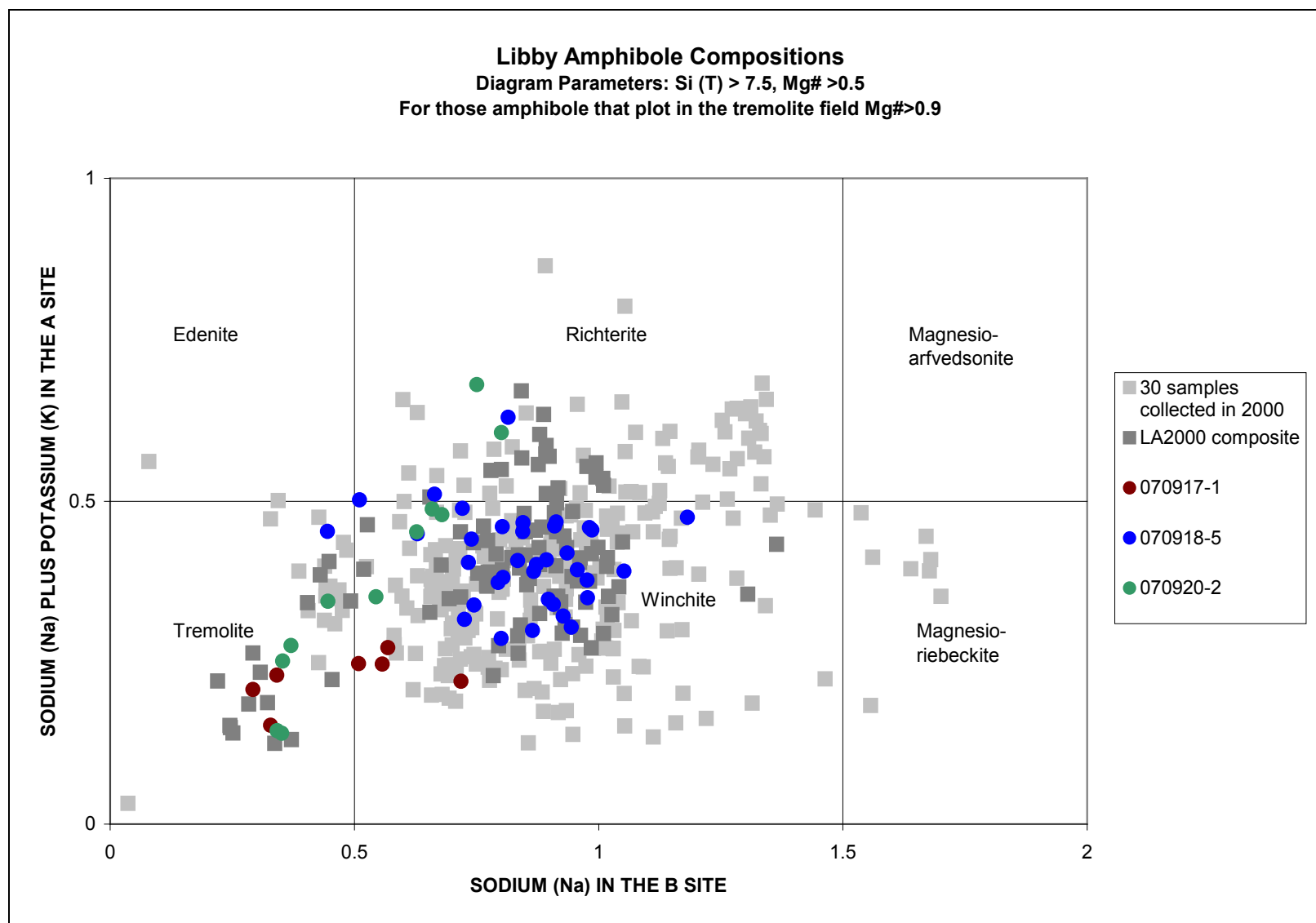
Figure 4. Electron-microprobe-determined amphibole compositions of the individual components of the LA2007 material compared to the original 30 samples collected in 2000 and the LA2000 composite material. Square legends symbols represent samples collected in 2000 and round symbols represent samples collected in 2007.
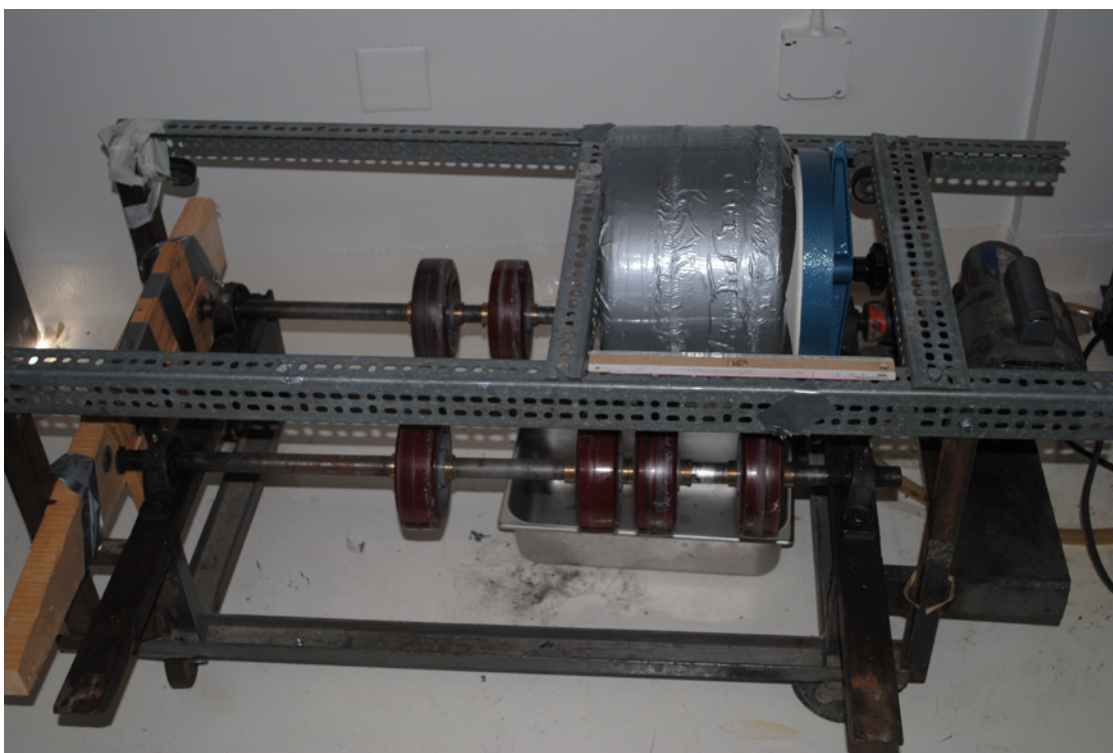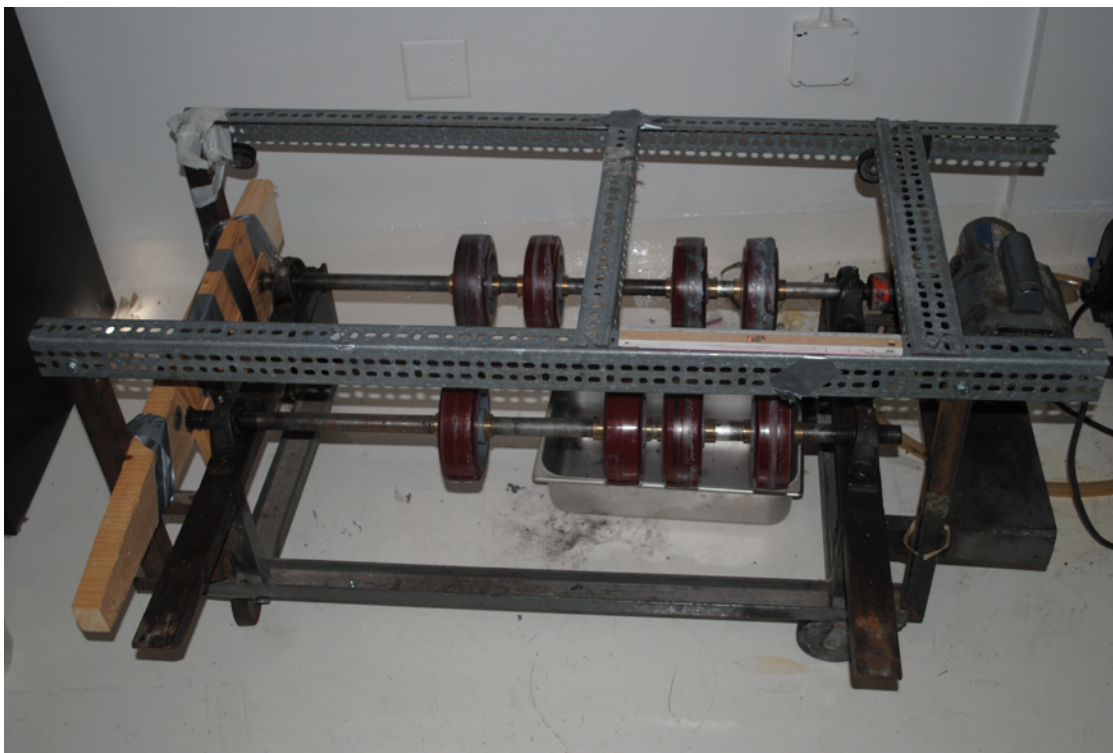
Figure 5. Customized roller mill. The steel grate holds the ball jar (wrapped in duct tape) in place.
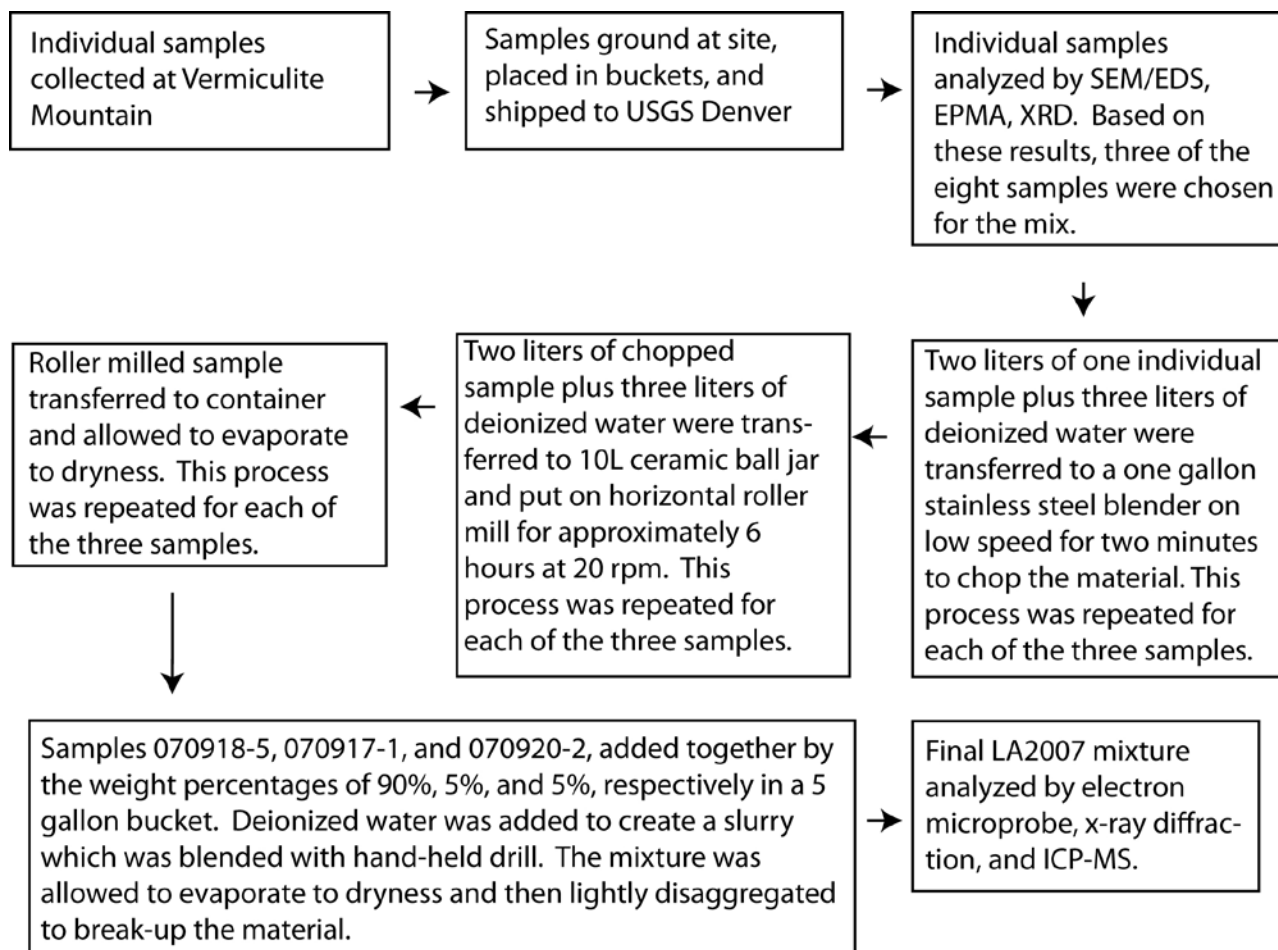
Figure 6. Work flow process for characterization and preparation of the LA2007 composite material. [SEM/EDS, Scanning Electron Microscope-Energy Dispersive Spectroscopy; EPMA, electron probe microanalysis; XRD, X-ray diffraction; L, liter; rpm, rotations per minute; ICP-MS, Inductively coupled plasma mass spectrometry]
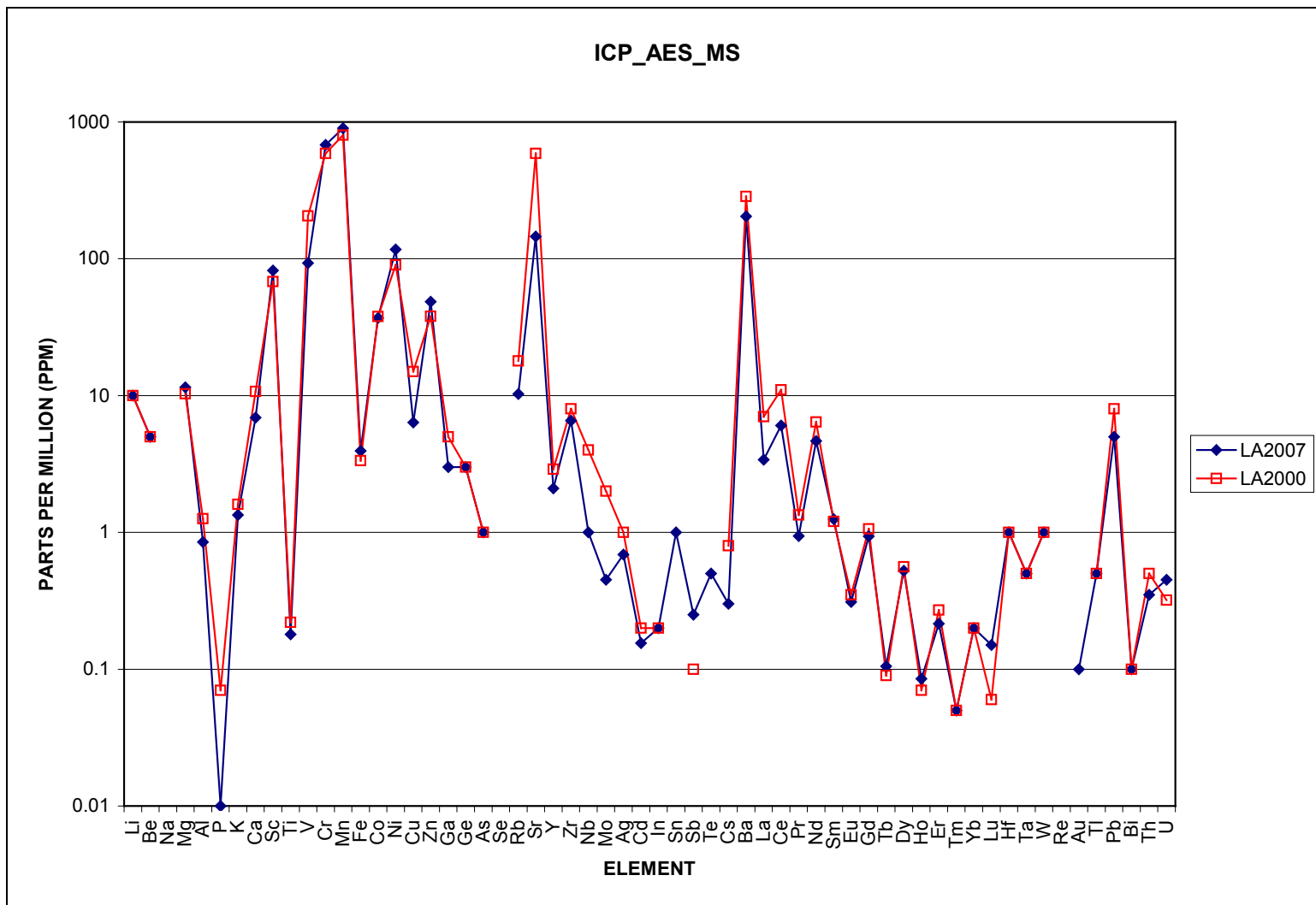
Figure 7. Comparison of bulk chemistry of LA2000 and LA2007 composite materials as determined by ICP-AES-MS.

Table 1. Sample numbers and locations referenced to the World Geodetic System WGS 1984 datum that comprise the LA2007 composite material.

May 2007 sample	Equivalent September 2007 sample	Long_WGS84	Lat_WGS84
USGS070531-11	070920-2	-115.406672	48.43606235
USGS070530-2	070917-1	-115.3982966	48.43273905
USGS070531-13-2	070918-5	-115.4008729	48.43804663

Table 2. Weight percentages of phases present in the individual components as well as the mixture based on x-ray diffraction analyses. In addition, trace amounts of titanite (CaTi SiO$_5$) were observed during electron microprobe analyses. [ND, nondetect]

Phase	General Formula	070917-1	070918-5	070920-2	LA2007-A	LA2007-B
Amphibole	(K,Na)(Na,Ca)$_2$(Mg,Fe)$_5$Si$_8$O$_{22}$(OH,F,Cl)$_2$	66	84	51	84	84
Calcite	CaCO$_3$	18	ND	24	3	4
Talc	Mg$_3$(Si$_4$O$_{10}$)(OH)$_2$	11	8	ND	2	1
Vermiculite	(Mg,Fe,Al)$_2$(Al,Si)$_4$O$_{10}$(OH)$_2$.4(H$_2$O)	5	ND	ND	ND	1
Orthoclase	KAlSi$_3$O$_8$	ND	7	5	7	8
Quartz	SiO$_2$	ND	ND	12	2	1
Dolomite	MgCa(CO$_3$)$_2$	ND	ND	5	1	1
Biotite	K(Mg,Fe)$_3$Al[Si$_3$O$_{10}$](OH,Cl,F)	ND	ND	3	ND	ND

Table 3. Bulk chemical analyses of the individual components of the LA2000 and LA2007 composite materials as well as aliquots of the LA2007 composite material (LA2007 A and LA2007 B). [ICP-MS, Inductively coupled plasma mass spectrometry; ICP-AES, Inductively coupled plasma atomic emission spectrometry; ICP-ACID, total acid digestion; ppm, parts per million; na, not applicable]

| | | | Year Analyzed | Feb 2010 | Feb 2010 | Feb 2010 | Feb 2010 | Feb 2010 | 2001 | 2001 | 2001 | 2001 | 2001 | 2001 | Dec 2010 | Jan 2011 |
| | | | Sample | LA2007 A | LA2007 B | 0709-18-5-win | 0709-20-2-ric | 0709-17-1-trem | 20B | 23B | 25B | 27B | 28B | 30B | LA2000 | LA2000 |
Bulk chemical method listed, other-wise ICP-MS-AES	Atomic Number	Element	Unit	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICPAES_MS_55
	3	Li	ppm	10	<10	<10	20	20	6.1	4	3	0.7	17	2	9.8	10
	4	Be	ppm	<5	<5	<5	<5	<5	0.2	0.4	2.1	0.8	1.8	0.4	4.8	<5
	11	Na	%	NA	NA	NA	NA	NA	0.83	1.4	1.8	0.85	1.8	2.5	2.03	na
	12	Mg	%	11.6	11.4	12.7	7.93	9.71	4.3	5.7	7.1	4.1	7.9	7.2	1.07	10.3
	13	Al	%	0.88	0.82	0.75	0.65	0.49	0.28	0.4	0.4	0.06	1.7	1	0.946	1.26
	15	P	%	0.01	0.01	0.01	<0.01	0.02	0.02	0.02	<0.01	0.04	<0.01	0.04	0.0665	0.07
	19	K	%	1.34	1.34	1.31	1.38	0.56	0.27	0.8	1	0.26	1.4	2.1	1.34	1.6
	20	Ca	%	6.94	6.88	6.49	12.8	11.3	16	14	8.5	20	3.9	4	1.01	10.7
	21	Sc	ppm	83	81	90	68	57	48	61	34	62	66	110	74.3	68
	22	Ti	%	0.18	0.18	0.21	0.15	0.14	0.1	0.07	0.1	0.1	0.2	0.2	0.207	0.22
	23	V	ppm	94	92	103	149	30	9	17	83	45	130	66	205	206
	24	Cr	ppm	680	680	710	1070	440	400	480	420	130	390	50	633	590
	25	Mn	ppm	900	900	900	800	800	590	610	410	460	500	740	875	800
	26	Fe	%	3.95	3.93	4.39	2.5	2.93	2.1	2.8	2.8	1.4	3.6	3.6	3.41	3.35
	27	Co	ppm	34.9	38.9	21.6	22.5	29.9	23	27	38	12	43	38	38.2	37.9
	28	Ni	ppm	118	116	124	78	92	43	46	110	26	88	49	86.9	90
C_ICP10	29	Cu	ppm	5.84	6.87	5.24	16.5	1.74	<3	10	6	20	8	<3	16.1	15
	30	Zn	ppm	52	45	46	50	39	10	20	30	10	51	30	50.4	38
	31	Ga	ppm	3	3	1	4	1	1.1	1.4	2.5	0.4	6.5	3.9	4.9	5
	32	Ge	ppm	3	3	2	2	3	1.2	2	2.2	1.6	1.2	1.9	na	3
C_ICP10	33	As	ppm	<1	<1	<1	<1	<1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	<30
C_Se Hyd	34	Se	ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<1	<1	<1	<1	<1	<1	na	na
	37	Rb	ppm	10.2	10.3	5.2	10.5	8.6	6.1	9.8	8.9	0.9	38	16	18.6	17.9
	38	Sr	ppm	149	142	42.9	1230	291	480	470	270	510	73	35	535	589
	39	Y	ppm	2	2.2	0.9	3.9	1.3	3.4	2.5	1.2	2.1	3.2	4.5	3.9	2.9
	40	Zr	ppm	6.6	6.5	2.6	10.8	2.8	na	na	na	na	na	na	na	8
	41	Nb	ppm	1	1	<1	3	<1	0.1	0.1	1.5	1	2.3	0.4	7.1	4

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	Atomic Number	Element	Year Analyzed	Feb 2010	Feb 2010	Feb 2010	Feb 2010	Feb 2010	2001	2001	2001	2001	2001	2001	Dec 2010	Jan 2011
			Sample	LA2007A	LA2007B	0709-18-5-win	0709-20-2-ric	0709-17-1-trem	20B	23B	25B	27B	28B	30B	LA2000	LA2000
Bulk chemical method listed, other-wise ICP-MS-AES			Unit	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICPAES_MS_55	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICP_ACID	ICPAES_MS_55
C_ICP10	42	Mo	ppm	0.6	0.3	0.3	0.5	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.05	<2
C_ICP10	47	Ag	ppm	0.73	0.65	0.46	2.19	0.55	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.028	<1
C_ICP10	48	Cd	ppm	0.16	0.15	0.15	0.2	0.11	< 0.1	0.1	< 0.1	0.1	0.1	< 0.1	<0.007	<0.2
	49	In	ppm	<0.2	<0.2	<0.2	<0.2	<0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	na	<0.2
	50	Sn	ppm	<1	<1	<1	<1	<1	< 0.5	< 0.5	0.7	0.8	0.6	< 0.5	na	25
	51	Sb	ppm	0.2	0.3	0.2	0.3	<0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	<0.04	0.1
C_Te Hyd	52	Te	ppm	<0.5	<0.5	<0.5	<0.5	<0.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	na	NA
	55	Cs	ppm	0.3	0.3	<0.1	0.3	0.6	0.7	0.2	0.2	0.2	2.1	0.2	0.87	0.8
	56	Ba	ppm	206	202	69.1	1570	195	64	120	47	47	560	370	294	285
	57	La	ppm	3.3	3.5	1.4	9.9	1.8	3.6	1.8	3.5	5.7	9.2	6.9	8.1	7
	58	Ce	ppm	5.8	6.3	2.8	13.9	4.3	8.6	5.4	4.7	6.4	12	14	12	11
	59	Pr	ppm	0.91	0.97	0.44	1.46	0.75	1.3	0.94	0.52	0.76	1.2	2.3	1.7	1.34
	60	Nd	ppm	4.5	4.8	2.4	6	3.9	6.9	5.2	2.3	3.8	5	12	7	6.4
	62	Sm	ppm	1.2	1.3	0.6	1.3	1.1	1.6	1.4	0.56	0.96	1	2.8	1.6	1.2
	63	Eu	ppm	0.28	0.34	0.15	0.3	0.24	0.44	0.38	0.16	0.27	0.3	0.74	0.42	0.35
	64	Gd	ppm	0.83	1.04	0.45	1.03	0.83	1.3	1	0.42	0.74	0.84	2	1.3	1.06
	65	Tb	ppm	0.11	0.1	<0.05	0.12	0.09	0.14	0.12	0.05	0.083	0.098	0.22	0.19	0.09
	66	Dy	ppm	0.52	0.53	0.27	0.61	0.34	0.74	0.6	0.26	0.42	0.59	1.1	0.75	0.56
	67	Ho	ppm	0.08	0.09	<0.05	0.12	0.06	0.13	0.1	0.04	0.071	0.11	0.18	0.14	0.07
	68	Er	ppm	0.2	0.23	0.07	0.35	0.15	0.31	0.22	0.11	0.18	0.3	0.39	0.46	0.27
	69	Tm	ppm	<0.05	<0.05	<0.05	<0.05	<0.05	0.04	0.03	0.02	0.02	0.04	0.055	0.065	<0.05
	70	Yb	ppm	0.2	0.2	0.1	0.4	0.1	0.2	0.2	0.09	0.1	0.3	0.3	0.36	0.2
	71	Lu	ppm	0.12	0.18	0.07	0.13	0.06	na	na	na	na	na	na	na	0.06
	72	Hf	ppm	<1	<1	<1	<1	<1	na	na	na	na	na	na	na	<1
	73	Ta	ppm	<0.5	<0.5	<0.5	<0.5	<0.5	na	na	na	na	na	na	na	<0.5
	74	W	ppm	<1	<1	<1	<1	<1	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.02	<1
	75	Re	ppm	na	na	na	na	na	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	na	NA
C_ICP10	79	Au	ppm	<0.1	<0.1	<0.1	<0.1	<0.1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	na	NA
	81	Tl	ppm	<0.5	<0.5	<0.5	<0.5	<0.5	0.1	< 0.1	< 0.1	0.2	0.3	0.5	0.21	<0.5
C_ICP10	82	Pb	ppm	5	5	4	7	2	2.1	2.4	4.2	1.9	3.7	3	8.92	8
	83	Bi	ppm	<0.1	<0.1	<0.1	<0.1	<0.1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	<0.06	<0.1

Bulk chemical method listed, other-wise ICP-MS-AES	Atomic Number	Element	Unit	Feb 2010	Feb 2010	Feb 2010	Feb 2010	Feb 2010	2001	2001	2001	2001	2001	2001	Dec 2010	Jan 2011
			Year Analyzed → Sample	LA2007 A	LA2007 B	0709-18-5-win	0709-20-2-ric	0709-17-1-trem	20B	23B	25B	27B	28B	30B	LA2000	LA2000
				ICPAES _MS_55	ICPAES _MS_55	ICPAES _MS_55	ICPAES _MS_55	ICPAES _MS_55	ICP_ACI D	ICP_ACI D	ICP_ACI D	ICP_ACI D	ICP_ACI D	ICP_ACI D	ICP_ACI D	ICPAES _MS_55
	90	Th	ppm	0.4	0.3	0.1	0.5	<0.1	0.08	< 0.06	0.1	< 0.06	0.44	0.2	0.55	0.5
	92	U	ppm	0.45	0.45	0.21	0.34	0.18	0.09	0.2	0.3	0.4	0.59	0.2	0.44	0.32

Table 4. Electron probe microanalysis of amphibole from the individual samples that compose the LA2007 mixture.
[Wt %, weight percent; AVG, average]

Wt %	070917-1 AVG (n=7)	2 Sigma	070918-5 AVG (n=32)	2 Sigma	070920-2 AVG (n=10)	2 Sigma
SiO_2	55.8	2.92	56.5	2.60	56.2	1.94
TiO_2	0.10	0.07	0.24	0.20	0.13	0.22
Al_2O_3	0.15	0.27	0.22	0.19	0.22	0.27
Cr_2O_3	NA	NA	0.07	0.04	0.23	0.21
FeO	4.88	3.02	5.81	0.67	3.13	2.08
MnO	0.09	0.06	0.09	0.04	0.11	0.05
MgO	20.8	3.05	20.6	0.88	21.8	1.57
CaO	9.56	2.42	7.13	1.32	9.12	2.24
Na2O	2.19	1.18	3.67	0.84	2.92	1.73
K2O	0.49	0.17	1.39	0.56	0.96	0.84
F	0.03	0.08	0.13	0.11	0.50	0.61
Cl	0.03	0.07	0.01	0.03	0.01	0.05
O=F,Cl	0.02	0.04	0.06	0.04	0.21	0.25
TOTAL	94.1	4.33	95.8	3.68	95.1	2.42

Structural Formula

	070917-1 AVG (n=7)	2 Sigma	070918-5 AVG (n=32)	2 Sigma	070920-2 AVG (n=10)	2 Sigma
Si	7.985	0.034	7.982	0.025	7.979	0.043
Al^{iv}	0.015	0.034	0.018	0.025	0.021	0.043
Sum T	8.000	0.000	8.000	0.000	8.000	0.000
Al^{vi}	0.010	0.010	0.019	0.017	0.016	0.023
Ti	0.011	0.008	0.025	0.020	0.014	0.024
Fe3+	0.231	0.268	0.374	0.324	0.121	0.109
Cr	0.000	0.000	0.005	0.009	0.010	0.030
Mg	4.443	0.443	4.331	0.173	4.621	0.221
Fe2+	0.306	0.229	0.246	0.209	0.216	0.215
Mn	0.000	0.000	0.000	0.001	0.001	0.006
Sum C	5.000	0.000	5.000	0.000	5.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000
Fe2+	0.051	0.138	0.067	0.139	0.035	0.063
Mn	0.011	0.007	0.011	0.005	0.012	0.009
Ca	1.464	0.311	1.080	0.212	1.386	0.334
Na	0.474	0.315	0.843	0.301	0.567	0.316
Sum B	2.000	0.000	2.000	0.000	2.000	0.000
Na	0.137	0.071	0.162	0.153	0.238	0.171
K	0.089	0.032	0.251	0.099	0.174	0.152
Sum A	0.226	0.077	0.412	0.149	0.412	0.307
Total Cation	15.226	0.077	15.412	0.149	15.412	0.307