# SUPPLEMENTARY INFORMATION

### Occurrence and characterization of tremolite asbestos from the Mid Atlantic Ridge

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**Figure S1.** Frames of the video taken during the rock sampling activity of the Nautile submarine. The images show the moment when the sample SMA1971-214 was collected.



**Figure S2.** Sample SMA1971-214 viewed under polarized light optical microscopy, (plane-polarized light). Tremolite fibres display a wavy orientation, with late kink cleavage and are commonly folded, suggesting deformation processes subsequent to crystallization. Fibres show the typical sigma-like structure.



**Figure S3.** Representative TEM and SEM images of the examined sample. **a**) TEM image of tremolite fibres. The white stars show the EDX analysis spots. **b**) SEM image of a tremolite fibres bundles as viewed perpendicular to the long axis of the fibres. **c**) Prismatic tremolite and lizardite aggregates. **d**) Close up of the lizardite cluster shown in (c); the image shows lizardite particles characterized by a non-fibrous habit. The black stars show the EDX analysis spots. **e**) TEM-EDX spectrum of the tremolite shown in (a). **f**) TEM-EDX spectrum of the lizardite shown in (d).



Figure S4. Thermal analysis and evolved gases mass spectrometry. a) TGA, DTG and DTA. b) MS-EGA.



**Figure S5.** a) Room Temperature Mössbauer spectrum of tremolite: blue line stands for Site 1, red line stands for Site 2. b) QSD distribution for ferrous site.



Figure S6. Crystal structure of tremolite asbestos of the SMA1971-214 sample projected onto (100).



**Figure S7.** Raman spectrum of the sample in the 200-1200 cm<sup>-1</sup> spectral range.



**Figure S8.** Raman spectrum of the studied tremolite (below) compared with the single-crystal FTIR spectrum (in red).



**Figure S9. a)** Major element composition of SMA1971-214 tremolite asbestos compared to amphiboles found in mafic and ultramafic rocks from different geodynamic contexts. Amphiboles from Vema gabbro and peridotite are from Brunelli *et al.*<sup>1</sup> and Cipriani *et al.*<sup>2</sup>, respectively. Others are from GEOROC<sup>3</sup> and EarthChem<sup>4</sup>. Calcium amphibole nomenclature according to Hawthorne *et al.*<sup>5</sup>. Cations are calculated based on 23 oxygens. **b**) Na+K in A site (a.p.f.u.) vs Al<sup>IV</sup> (a.p.f.u.). **c**) TiO<sub>2</sub> (wt.%) vs Al<sup>IV</sup> (a.p.f.u.); isotherms are from Ernst and Lui<sup>6</sup>. **d**) Al/(Al+Si) in T site (a.p.f.u.) vs Al/(Al+Mg+Fe) in C site (a.p.f.u.).  $\pm 1 \sigma$  compositional variability of tremolite SMA1971-214 is within the symbol area (see also Table S2 for standard deviation values).

		Percentiles							
	Min	$5^{\text{th}}$	$25^{\text{th}}$	50 <sup>th</sup>	75 <sup>th</sup>	95 <sup>th</sup>	Max	σ	$\overline{\mathbf{x}}$
L (µm)	5.12	7.33	10.6	16.1	22.1	73.0	93.4	19.6	22.3
W (µm)	0.17	0.29	0.54	1.05	1.57	2.68	3.03	0.72	1.17
L/D	4.76	5.68	10.7	17.0	30.0	75.4	96.3	22.7	24.6

**Table S1.** Summary statistics of the geometry of tremolite fibres. L (length); W (width); Min (minimum); Max (maximum);  $\sigma$  (standard deviation);  $\bar{x}$  (average).

	Wt%	σ
SiO <sub>2</sub>	54.21	0.58
TiO <sub>2</sub>	0.09	0.03
Al <sub>2</sub> O <sub>3</sub>	3.73	0.32
Cr <sub>2</sub> O <sub>3</sub>	0.44	0.20
MnO	0.07	0.03
MgO	22.44	0.41
CaO	12.10	0.32
Na <sub>2</sub> O	1.03	0.11
K <sub>2</sub> O	0.02	0.01
NiO	0.10	0.03
FeO <sub>tot</sub>	2.59	0.21
PbO	0.03	0.01
CoO	0.03	0.02
$V_2O_5$	0.04	0.02
CuO	0.06	0.04
F	bdl	-
Cl	bdl	-
Total:	96.98	0.36

**Table S2.** Average chemical composition of samples from EMPA analysis. Reported chemical compositions are mean values of several analyses carried out on 33 EMPA spot analyses. Wt% (weight percent);  $\sigma$  (standard deviation); bdl (below detection limit).

	$\delta_0 (mm/s)$	$\delta_1 (\text{mm/s})$	<Δ>(mm/s)	$\sigma_{\Delta}$ (mm/s)	p (%)	A (%)
Site 1	$0.26 \pm 0.07$		1.13±0.09	$0.2 \pm 0.08$	100	12±3
S:40 3	1.07+0.05	$0.02 \pm 0.02$	2.73±0.05	$0.29 \pm 0.06$	52	0012
Site 2	$1.0/\pm 0.05$ 0	$0.03\pm0.02$	1.79±0.03	$0.19 \pm 0.04$	48	88±3

**Table S3.** Hyperfine parameters calculated from the tremolite spectrum,  $\chi^2$ : 0.65, d0, center shift,  $\delta_1$ , coupling parameters between the center shift and the quadrupole splitting,  $\langle \Delta \rangle$  the average quadurpole splitting of the component,  $\sigma_{\Delta}$  the Gaussian width of the component, p the weight of the component, A relative area.

Identification code	ShelxL
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>m</i>
Unit cell dimensions	a = 9.8469(6)  Å
	b = 18.0651(11) Å
	c = 5.2795(4)  Å
	$\beta = 104.803(3)^{\circ}$
Volume	907.98(9) Å <sup>3</sup>
Ζ	2
Crystal size	0.01 x 0.03 x 0.2 mm
θ range for data collection	3.992-29.99°.
Index ranges	-13<=h<=1325<=k<=24. -7<=l<=7
Reflections collected	11055
Independent reflections	1276 [R(int) = 0.0355]
Completeness to $\Theta = 25.24^{\circ}$	99.1 %
Absorption correction	SADABS multiscan
Max. and min. transmission	0.7469-0.6349
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1276 / 0 / 108
Goodness-of-fit on F <sup>2</sup>	0.694
Final R <sub>1</sub> indices obs. all data	0.030. 0.032
Largest diff. peak and hole	1.213 and -0.916 e <sup>-</sup> .Å <sup>-3</sup>

 Table S4. Crystal data and structure refinement for SMA1971-214 tremolite asbestos.

Site	Occupancy	Х	У	Z	$U_{eq}$
Α	Na <sub>0.29</sub>	0	1/2	0	0.128(14)
<i>M</i> (1)	Mg <sub>0.96</sub> Fe <sub>0.04</sub>	0	0.08813(6)	1/2	0.00674 (39)
<i>M</i> (2)	Mg <sub>0.96</sub> Fe <sub>0.04</sub>	0	0.17645(6)	0	0.00652 (39)
<i>M</i> (3)	Mg <sub>0.96</sub> Fe <sub>0.04</sub>	0	0.0	0	0.00602 (55)
<i>M</i> (4)	Ca <sub>0.96</sub>	0	0.27780(11)	1/2	0.01041(28)
<i>M</i> (4')	Fe <sub>0.04</sub>	0	0.2519(27)	1⁄2	0.030(8)
<i>T</i> (1)	Si <sub>0.88</sub> Al <sub>0.12</sub>	0.28048(7)	0.08425(4)	0.29753(12)	0.00623(16)
<i>T</i> (2)	Si 1	0.28922(7)	0.17143(4)	-0.19456(12)	0.00653(16)
O(1)	01	0.11042(18)	0.08624(10)	0.21774(32)	0.00860(33)
O(2)	01	0.11910(17)	0.17168(10)	0.72508(32)	0.00842(33)
O(3)	01	0.10952(27)	0	0.71537(48)	0.01040(47)
O(4)	01	0.13385(19)	0.25176(10)	0.20990(34)	0.01115(34)
O(5)	01	0.34730(18)	0.13575(10)	0.10187(33)	0.01119(35)
O(6)	01	0.34404(18)	0.11736(10)	0.59423(33)	0.01094(35)
O(7)	01	0.33803(27)	0	0.28505(52)	0.01217(49)
Н	H 1	0.19091	0.01300	0.76970	0.140(27)

**Table S5**. Fractional atomic, refined occupancies and displacement coordinates for SMA1971-214 tremolite asbestos.

T(1) Si <sub>0.88</sub> Al <sub>0.12</sub>		<i>T</i> (2) Si <sub>1</sub>	
O(1)	1.619(2)	O(4)	1.593(2)
O(7)	1.631(1)	O(2)	1.619(2)
O(6)	1.644(2)	O(5)	1.654(2)
O(5)	1.647(2)	O(6)	1.672(2)
<71-0>	1.635	<72-0>	1.635
QE	1.0012	QE	1.0048
AV	5.28	AV	19.43
$M(1) Mg_{0.96}Fe_{0.04}$		M(2) Mg <sub>0.96</sub> Fe <sub>0.04</sub>	
O(1) x2	2.057(2)	O(4) x2	2.017(2)
O(2) x2	2.087(2)	O(2) x2	2.088(2)
O(3) x3	2.089(2)	O(1) x2	2.126(2)
< <i>M</i> (1)-O>	2.078	<i><m< i="">(2)-O&gt;</m<></i>	2.077
QE	1.0112	QE	1.0071
AV	36.64	AV	22.56
$M(3) \mathrm{Mg}_{0.96}\mathrm{Fe}_{0.04}$		<i>M</i> (4) Ca <sub>0.96</sub>	
O(3) x2	2.061(2)	O(4) x2	2.310(2)
O(1) x4	2.072(2)	O(2) x2	2.398(2)
		O(6) x2	2.566(2)
		O(5) x2	2.739(2)
<i><m< i="">(3)-O&gt;</m<></i>	2.068	<i><m< i="">(4)-O&gt;</m<></i>	2.503
QE	1.0147		
AV	47.70		
A Na <sub>0.29</sub>		<i>M</i> (4') Fe <sub>0.04</sub>	
O(7) x2	2.457(3)	O(2) x2	2.04(3)
O(5) x4	2.996(2)	O(4) x2	2.262(2)
O(6) x4	3.124(2)	O(6) x2	2.93(4)
<a-o></a-o>	2.939	< <i>M</i> (4')-O>	2.411
<i>T</i> (1)	O(5)	<i>T</i> (2)	135.8(1)
<i>T</i> (1)	O(6)	<i>T</i> (2)	137.6(1)
<i>T</i> (1)	O(7)	<i>T</i> (1)	137.8(3)
O(5)	O(6)	O(5)	165.6(1)
O(6)	O(7)	O(6)	105.3(1)

**Table S6.** Refined occupancies, selected bond distances (Å) and angles (°) for coordination polyhedral in SMA1971-214 tremolite asbestos. Quadratic elongation (QE) and bond angle variance (AV), are reported following by Robinson et al.<sup>7</sup>.

	<i>T</i> (1)	<i>T</i> (2)	<i>M</i> (1)	<i>M</i> (2)	<i>M</i> (3)	<i>M</i> (4)	Α	Н	Σ	∑(H)
O(1)	1.022		$0.752^{x2}$	0.638 <sup>x2</sup>	1.444 <sup>x4</sup>				2.08	
O(2)		1.012	$0.692^{x2}$	$0.686^{x2}$		$0.596^{x^2}$			2.00	
O(3)			$0.688^{x2}$		$0.742^{x2}$			0.81	1.06	1.86
O(4)		1.088		0.810 <sup>x2</sup>		$0.756^{x^2}$			1.87	
O(5)	0.948	0.923				$0.238^{x2}$	$0.039^{x2}$		2.01	
O(6)	0.957	0.877				$0.378^{x2}$	$0.039^{x2}$		2.04	
O(7)	$0.990^{x^2}$						$0.085^{x2}$	0.19	2.02	2.213
Σ	3.92	3.90	2.13	2.13	2.19	1.97	0.16	1		
Table S	Table S7. Bond-valence analysis (v.u.) for SMA1971-214 tremolite asbestos, based on the EPMA									

occupancies calculated following Brese and O'Keeffe<sup>8</sup>. The contribution of the O–H bond has been evaluated according to Ferraris and Ivaldi<sup>9</sup>.

(1)	(2)
cm <sup>-1</sup>	cm <sup>-1</sup>
1063	1062
1030	1031
950	950
933	932
746	751
674	676
580	-
532	531
518	516
-	438
419	418
395	396
372	373
308	306
253	254
235	234
223	225

**Table S8.** Raman bands position for tremolite in the region 1200-200 cm<sup>-1</sup>. (1) = this study. (2) = tremolite from Rinaudo et al.<sup>10</sup>.

	Chl	orite	Lizardite		
	Wt%	σ	Wt%	σ	
SiO <sub>2</sub>	31.49	0.33	38.00	0.87	
Al <sub>2</sub> O <sub>3</sub>	16.02	0.01	5.86	1.28	
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.05	0.43	0.25	
MnO	1.58	0.05	0.02	0.01	
MgO	16.88	0.10	36.51	1.52	
CaO	0.19	0.15	0.08	0.02	
Na <sub>2</sub> O	0.02	0.03	0.01	0.01	
K <sub>2</sub> O	0.02	0.01	0.01	0.01	
NiO	0.01	0.03	0.06	0.01	
FeO	23.61	0.38	4.05	0.64	
Total	89.86	0.46	85.21	0.59	

Table S9. Major element composition of chlorite and lizardite. Data obtained from EPMA analysis

#### Serpentine discrimination

Serpentine minerals chrysotile, lizardite and antigorite are stable under a wide range of temperatures and pressures<sup>11-13</sup>. Lizardite and chrysotile are stable at low-pressure low-temperature conditions (0–300 °C, < 1.0 GPa), but lizardite is usually more stable than chrysotile<sup>13</sup>. Antigorite is the high-pressure and high-temperature stable serpentine. Both experimental and natural observations show that the lizardite to antigorite transition starts at about 300 °C, with P> 0.7 GPa, with a complete transformation to antigorite near 400 °C<sup>13</sup>.

Among the minerals of the serpentine only chrysotile shows a fibrous aspect<sup>11</sup> In addition, chrysotile is poor in Al and Fe, while antigorite and lizardite are enriched in Fe<sup>+3</sup> and Al<sup>11</sup>. The serpentine found in the SMA1971-214 shows non-fibrous habit (Fig. 3S) and its Al content (> 5.0 wt%) is similar to that of lizardite and antigorite<sup>14</sup> (Table S9). On the assumption that sample SMA1971-214 was developed in a low temperature and pressure regime (see the main text of the manuscript), antigorite can be excluded, and the serpentine in the sample SMA1971-214 can be guessed as lizardite.

#### Structure refinement of tremolite.

A total of 1768 frames were collected, using  $\varphi$  and  $\omega$  scan modes, with an exposure time of 30s per frame. Intensity data were integrated and corrected for Lorentz, polarization, background effects, and absorption using the APEX 3 software package<sup>15</sup>. The total exposure time was 14.73 h. The integration of the data using a monoclinic unit cell yielded a total of 12016 reflections to a maximum  $\theta$  angle of 29.99° (0.71 Å resolution). Scattering curves for neutral atoms were taken from the International Tables for Crystallography<sup>16</sup>. The final cell constants a = 9.8469(6) Å. b = 18.0651(11) Å. c = 5.2795(4) Å.  $\beta = 104.803(3)^\circ$ . V = 907.98(9) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 7068 reflections above 20  $\sigma$ (I) with 4.51° < 20 < 29.99°. Structural model for tremolite as reported by Yang & Evans<sup>17</sup> was assumed as a starting one for structural refinement. Several cycles of isotropic refinement led to R1 = 0.11 confirming the correctness of the structural model. Mixed occupancies by Mg and Fe for M(1), M(2) and M(3) sites and Si and A1 for T(1) site were then refined., with the constrain of full occupancy. Some further cycles of anisotropic refinement allowed then to identify in the Fourier difference maps peaks corresponding to M(4') split site, A site and H site. Following literature studies<sup>17-19</sup> an occupancy by Fe was assumed for M(4') site, refining an isotropic displacement parameter and constraining the sum of M(4') and M(4) occupancies to full occupancy. An occupancy by Na for A site was assumed and allowed to vary unconstrained, together with an isotropic displacement parameter. H site was assumed as fully occupied, holding fixed its positional parameters derived from the Fourier difference maps, and refining an isotropic displacement parameter.

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## References relating to Figure 4 present in the main text

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