

Online Resource 4: Sulphur Speciation Measurements

Fitted Curve Parameters

Sample Number	Spectrometer	A	α	ξ	ω	δ	R ²	Peak Position (sin θ)	Peak Position SD (sin θ)	Analysis Date
Troilite 1	3	32530.97	2.06	61427.55	71.05	385.28	0.999	61465.07	0.42	March 27, 2024 10:42:14 AM
Troilite 1	4	18237.08	0.68	61443.00	49.17	103.45	0.998	61463.91	0.50	March 27, 2024 10:42:14 AM
Troilite 1	5	15224.31	-1.45	61487.63	62.41	104.79	0.999	61453.81	0.51	March 27, 2024 10:42:14 AM
Troilite 2	3	32743.32	2.03	61428.56	70.90	384.38	0.999	61466.08	0.37	March 27, 2024 12:27:23 PM
Troilite 2	4	18112.24	0.71	61442.06	49.81	102.14	0.999	61463.68	0.46	March 27, 2024 12:27:23 PM
Troilite 2	5	15363.61	-1.41	61487.19	61.98	103.60	0.999	61453.66	0.55	March 27, 2024 12:27:23 PM
Troilite 3	3	32765.91	2.07	61428.51	70.98	387.99	0.999	61465.96	0.40	March 27, 2024 1:54:59 PM
Troilite 3	4	18167.89	0.69	61442.99	49.65	102.39	0.999	61464.23	0.51	March 27, 2024 1:54:59 PM
Troilite 3	5	15234.48	-1.45	61487.99	62.55	102.57	0.999	61454.09	0.56	March 27, 2024 1:54:59 PM
Troilite 4	3	32638.29	2.06	61428.75	70.83	389.82	0.999	61466.14	0.43	March 27, 2024 3:07:18 PM
Troilite 4	4	18437.26	0.65	61444.33	48.85	103.18	0.999	61464.51	0.43	March 27, 2024 3:07:18 PM
Troilite 4	5	15105.15	-1.46	61488.15	62.74	103.79	0.999	61454.14	0.60	March 27, 2024 3:07:18 PM
Troilite 5	3	32751.88	2.06	61428.74	70.90	386.91	0.999	61466.19	0.38	March 27, 2024 4:15:04 PM
Troilite 5	4	20520.64	0.00	61464.97	44.09	102.32	0.999	61464.93	0.48	March 27, 2024 4:15:04 PM
Troilite 5	5	15316.57	-1.41	61487.59	62.03	105.34	0.999	61454.03	0.58	March 27, 2024 4:15:04 PM
Troilite 6	3	32673.56	2.06	61427.85	70.86	385.35	0.999	61465.28	0.38	March 27, 2024 5:29:54 PM
Troilite 6	4	18409.21	0.65	61443.32	49.04	102.31	0.999	61463.57	0.41	March 27, 2024 5:29:54 PM
Troilite 6	5	15230.45	-1.44	61487.33	62.56	103.79	0.999	61453.44	0.58	March 27, 2024 5:29:54 PM
Troilite 7	3	32659.86	2.05	61428.02	70.90	386.66	0.999	61465.48	0.38	March 27, 2024 7:15:11 PM
Troilite 7	4	18322.97	0.68	61443.01	49.38	103.19	0.999	61463.96	0.43	March 27, 2024 7:15:11 PM
Troilite 7	5	15268.10	-1.42	61487.17	62.33	103.41	0.999	61453.43	0.56	March 27, 2024 7:15:11 PM
Troilite 8	3	32810.01	2.04	61429.53	70.90	385.98	0.999	61467.05	0.41	March 28, 2024 9:03:18 AM
Troilite 8	4	18390.90	0.66	61444.70	48.83	104.27	0.999	61464.96	0.45	March 28, 2024 9:03:18 AM
Troilite 8	5	15267.60	-1.45	61488.40	62.71	103.85	0.999	61454.42	0.58	March 28, 2024 9:03:18 AM
Troilite 9	3	32555.79	2.08	61428.11	71.22	385.13	0.999	61465.65	0.44	March 28, 2024 11:24:36 AM
Troilite 9	4	18184.89	0.70	61442.51	49.52	102.62	0.999	61463.89	0.48	March 28, 2024 11:24:36 AM
Troilite 9	5	15120.26	-1.47	61488.34	63.05	103.39	0.999	61454.15	0.47	March 28, 2024 11:24:36 AM

Table OR4.1. Summary of fitted skewed Gaussian curve parameters and calculated peak positions for troilite SK α wavelength scans. SD = Standard deviation of peak position for 1000 bootstrap samples. See Online Resource 3 for details of curve fitting procedure and bootstrap uncertainty estimations.

Sample Number	Spectrometer	A	α	ξ	ω	δ	R^2	Peak Position (sin θ)	Peak Position SD (sin θ)	Analysis Date
Troilite 10	3	32513.17	2.07	61428.09	71.11	385.94	0.999	61465.60	0.42	March 28, 2024 1:14:16 PM
Troilite 10	4	18686.78	0.59	61445.71	48.03	103.38	0.999	61464.32	0.49	March 28, 2024 1:14:16 PM
Troilite 10	5	15245.83	-1.43	61488.18	62.72	103.13	0.999	61454.21	0.56	March 28, 2024 1:14:16 PM
Troilite 11	3	32563.33	2.07	61427.89	71.13	388.77	0.999	61465.42	0.44	March 28, 2024 3:38:51 PM
Troilite 11	4	18590.89	0.62	61444.58	48.49	103.55	0.999	61463.92	0.47	March 28, 2024 3:38:51 PM
Troilite 11	5	15209.43	-1.46	61488.21	62.71	104.69	0.999	61454.22	0.47	March 28, 2024 3:38:51 PM
Troilite 12	3	32801.68	2.04	61425.78	70.81	388.07	0.999	61463.25	0.38	March 28, 2024 6:02:48 PM
Troilite 12	4	20493.74	0.00	61462.08	44.11	102.63	0.999	61462.00	0.48	March 28, 2024 6:02:48 PM
Troilite 12	5	15272.06	-1.44	61485.74	62.85	102.40	0.999	61451.69	0.60	March 28, 2024 6:02:48 PM
Troilite 13	3	32859.20	2.05	61426.23	70.76	389.99	0.999	61463.63	0.40	March 28, 2024 7:48:00 PM
Troilite 13	4	18365.24	0.68	61440.91	49.27	101.47	0.999	61461.80	0.43	March 28, 2024 7:48:00 PM
Troilite 13	5	15153.57	-1.47	61486.74	63.13	104.40	0.999	61452.52	0.59	March 28, 2024 7:48:00 PM
Troilite 14	3	32865.79	2.04	61426.96	70.59	388.89	0.999	61464.31	0.42	March 28, 2024 9:39:34 PM
Troilite 14	4	18611.68	0.62	61443.17	48.53	103.38	0.999	61462.68	0.50	March 28, 2024 9:39:34 PM
Troilite 14	5	15291.81	-1.43	61486.60	62.58	104.45	0.999	61452.71	0.62	March 28, 2024 9:39:34 PM

Table OR4.1. (Continued)

Sample Number	Spectrometer	A	α	ξ	ω	δ	R^2	Peak Position (sin θ)	Peak Position SD (sin θ)	$\Delta SK\alpha$ (sin θ)	$\Delta SK\alpha$ Uncertainty (sin θ)	Analysis Date
Anhydrite 1	3	21604.69	2.05	61392.93	71.86	237.19	0.999	61430.90	0.51	34.68	1.16	March 27, 2024 10:58:55 AM
Anhydrite 1	4	11852.57	0.77	61405.71	51.01	60.92	0.999	61428.87	0.51	34.93	1.23	March 27, 2024 10:58:55 AM
Anhydrite 1	5	10167.05	-1.38	61452.85	62.46	60.66	0.999	61419.10	0.36	34.63	1.03	March 27, 2024 10:58:55 AM
Anhydrite 2	3	21497.20	2.04	61393.35	71.32	242.76	0.999	61431.09	0.38	35.18	0.94	March 27, 2024 7:27:39 PM
Anhydrite 2	4	11729.48	0.78	61405.72	50.96	62.09	0.999	61428.96	0.59	35.49	1.33	March 27, 2024 7:27:39 PM
Anhydrite 2	5	10011.40	-1.44	61453.12	62.75	62.35	0.999	61419.13	0.43	34.79	1.17	March 27, 2024 7:27:39 PM
Anhydrite 4	3	21554.33	2.04	61392.15	71.68	241.34	0.999	61430.07	0.42	34.24	1.04	March 28, 2024 9:50:46 PM
Anhydrite 4	4	11746.80	0.77	61404.99	51.24	60.67	0.999	61428.18	0.51	34.50	1.24	March 28, 2024 9:50:46 PM
Anhydrite 4	5	10163.01	-1.36	61451.75	62.47	60.70	0.999	61418.05	7.25	34.66	14.53	March 28, 2024 9:50:46 PM

Table OR4.2. Summary of fitted skewed Gaussian curve parameters, calculated peak positions and $\Delta SK\alpha$ values for anhydrite $SK\alpha$ wavelength scans. SD = Standard deviation of peak position for 1000 bootstrap samples. See Online Resource 3 for details of curve fitting procedure and uncertainty estimations.

Sample Number	Spectrometer	A	α	ξ	ω	δ	R ²	Peak Position (sin θ)	Peak Position SD (sin θ)	$\Delta SK\alpha$ (sin θ)	$\Delta SK\alpha$ Uncertainty (sin θ)	S ⁶⁺ /S ^{total}	S ⁶⁺ /S ^{total} Uncertainty	Analysis Date
Pyrite 1	3	48536.78	2.10	61424.97	71.29	576.16	0.999	61462.47	0.37	3.11	0.92	0.09	0.03	March 27, 2024 11:13:46 AM
Pyrite 1	4	26611.89	0.78	61437.53	50.50	151.70	0.999	61460.61	0.46	3.19	1.14	0.09	0.03	March 27, 2024 11:13:46 AM
Pyrite 1	5	22772.51	-1.44	61484.63	62.23	156.54	0.999	61450.93	0.42	2.81	1.10	0.08	0.03	March 27, 2024 11:13:46 AM
Pyrite 2	3	48604.49	2.11	61425.25	71.27	576.28	0.999	61462.71	0.40	3.56	0.97	0.10	0.03	March 27, 2024 7:41:04 PM
Pyrite 2	4	26912.83	0.71	61439.45	49.96	151.43	0.999	61461.24	0.40	3.21	1.03	0.09	0.03	March 27, 2024 7:41:04 PM
Pyrite 2	5	22858.13	-1.39	61484.39	61.96	155.66	0.999	61450.9	0.40	3.02	1.15	0.09	0.03	March 27, 2024 7:41:04 PM
Pyrite 3	3	48580.63	2.09	61426.62	71.30	573.21	0.999	61464.14	0.42	2.12	1.01	0.06	0.03	March 28, 2024 8:46:22 AM
Pyrite 3	4	27162.87	0.69	61441.25	49.42	153.80	0.999	61462.4	0.45	2.05	1.11	0.06	0.03	March 28, 2024 8:46:22 AM
Pyrite 3	5	22820.76	-1.42	61485.42	62.34	156.16	0.999	61451.69	0.42	2.23	1.18	0.06	0.03	March 28, 2024 8:46:22 AM
Pyrite 4	3	48653.13	2.08	61424.86	71.13	574.88	0.999	61462.36	0.35	1.95	0.94	0.06	0.03	March 28, 2024 10:02:05 PM
Pyrite 4	4	26953.96	0.71	61439.01	49.75	152.52	0.999	61460.69	0.45	1.99	1.13	0.06	0.03	March 28, 2024 10:02:05 PM
Pyrite 4	5	22744.80	-1.45	61485.06	62.49	154.83	0.999	61451.2	0.36	1.50	1.17	0.04	0.03	March 28, 2024 10:02:05 PM

Table OR4.3. Summary of fitted skewed Gaussian curve parameters, calculated peak positions, $\Delta SK\alpha$ values and calculated S⁶⁺/S^{total} values for pyrite SK α wavelength scans. SD = Standard deviation of peak position for 1000 bootstrap samples. See Online Resource 3 for details of curve fitting procedure and uncertainty estimations.

Sample Number	Spectrometer	A	α	ξ	ω	δ	R ²	Peak Position (sin θ)	Peak Position SD (sin θ)	$\Delta SK\alpha$ (sin θ)	$\Delta SK\alpha$ Uncertainty (sin θ)	S ⁶⁺ /S ^{total}	S ⁶⁺ /S ^{total} Uncertainty	Analysis Date
TAN1213-45-3-A-a	3	122.52	1.92	61400.81	74.31	9.87	0.993	61440.49	1.52	25.09	3.08	0.72	0.09	March 27, 2024 11:32:08 AM
TAN1213-45-3-A-a	4	57.25	1.20	61403.33	60.65	3.76	0.986	61435.46	1.71	28.34	3.48	0.81	0.10	March 27, 2024 11:32:08 AM
TAN1213-45-3-A-a	5	58.29	-1.13	61458.50	61.87	3.98	0.988	61426.13	1.20	27.60	2.52	0.80	0.08	March 27, 2024 11:32:08 AM
TAN1213-45-3-E-b	3	96.17	1.88	61403.51	74.81	9.64	0.993	61443.59	1.15	22.44	2.36	0.65	0.07	March 27, 2024 1:00:48 PM
TAN1213-45-3-E-b	4	49.49	1.01	61410.07	57.47	3.73	0.984	61439.22	1.58	24.74	3.23	0.71	0.10	March 27, 2024 1:00:48 PM
TAN1213-45-3-E-b	5	48.92	-0.97	61458.08	60.28	3.91	0.992	61427.84	0.87	26.04	1.91	0.75	0.06	March 27, 2024 1:00:48 PM
TAN1213-45-3-G-a	3	183.49	1.36	61408.95	69.04	10.23	0.998	61446.19	0.79	19.86	1.68	0.57	0.05	March 27, 2024 2:11:37 PM
TAN1213-45-3-G-a	4	100.29	-0.01	61441.19	49.17	3.83	0.994	61440.97	0.95	23.40	2.02	0.67	0.06	March 27, 2024 2:11:37 PM
TAN1213-45-3-G-a	5	84.49	-1.05	61459.97	63.48	3.96	0.995	61427.35	0.91	26.77	2.00	0.77	0.06	March 27, 2024 2:11:37 PM
TAN1213-45-3-J-a	3	131.01	1.86	61404.85	73.15	10.18	0.995	61444.10	0.93	22.06	1.94	0.63	0.06	March 27, 2024 3:21:18 PM
TAN1213-45-3-J-a	4	63.78	1.10	61408.18	60.93	3.80	0.992	61439.85	1.11	24.87	2.31	0.70	0.07	March 27, 2024 3:21:18 PM
TAN1213-45-3-J-a	5	60.50	-1.37	61468.05	66.64	3.95	0.992	61432.07	0.86	22.01	1.91	0.63	0.06	March 27, 2024 3:21:18 PM
TAN1213-45-3-L-a	3	97.19	1.65	61402.64	72.78	9.50	0.995	61442.08	1.12	23.65	2.31	0.67	0.07	March 27, 2024 4:36:03 PM
TAN1213-45-3-L-a	4	53.49	-0.58	61459.77	51.77	3.71	0.985	61439.91	1.57	24.34	3.20	0.69	0.09	March 27, 2024 4:36:03 PM
TAN1213-45-3-L-a	5	45.16	-1.31	61462.78	65.92	3.90	0.985	61427.36	1.40	26.37	2.91	0.76	0.09	March 27, 2024 4:36:03 PM
TAN1213-45-3-R-a	3	111.08	2.08	61401.82	76.78	9.76	0.994	61442.29	1.40	23.08	2.86	0.66	0.08	March 27, 2024 6:20:24 PM
TAN1213-45-3-R-a	4	58.32	0.87	61413.59	57.18	3.73	0.986	61441.12	1.49	22.65	3.03	0.64	0.09	March 27, 2024 6:20:24 PM
TAN1213-45-3-R-a	5	57.72	-1.01	61457.82	58.93	3.96	0.987	61427.89	1.38	25.54	2.88	0.73	0.09	March 27, 2024 6:20:24 PM

Table OR4.4. Summary of fitted skewed Gaussian curve parameters, calculated peak positions, $\Delta SK\alpha$ values and calculated S⁶⁺/S^{total} values for SK α wavelength scans of basaltic melt inclusions. SD = Standard deviation of peak position for 1000 bootstrap samples. See Online Resource 3 for details of curve fitting procedure and uncertainty estimations.

Sample Number	Spectrometer	A	α	ξ	ω	δ	R^2	Peak Position (sin θ)	Peak Position SD (sin θ)	$\Delta SK\alpha$ (sin θ)	$\Delta SK\alpha$ Uncertainty (sin θ)	S^{6+}/S^{total}	S^{6+}/S^{total} Uncertainty	Analysis Date
SO253-081-12B-R-a	3	24.81	1.36	61397.90	71.26	7.86	0.973	61436.34	2.26	27.63	4.57	0.81	0.14	March 28, 2024 8:06:31 PM
SO253-081-12B-R-a	4	10.43	-1.53	61471.02	62.71	3.26	0.918	61436.99	3.10	25.26	6.23	0.73	0.18	March 28, 2024 8:06:31 PM
SO253-081-12B-R-a	5	10.45	-1.25	61462.64	70.58	3.31	0.944	61424.96	2.53	27.65	5.14	0.80	0.15	March 28, 2024 8:06:31 PM
U1529A-1R-1-W-I-a	3	22.64	1.31	61411.00	66.44	8.14	0.967	61446.69	2.09	18.94	4.22	0.55	0.12	March 28, 2024 11:41:38 AM
U1529A-1R-1-W-I-a	4	9.39	-1.27	61483.55	66.08	3.26	0.924	61448.20	4.37	15.91	8.77	0.46	0.25	March 28, 2024 11:41:38 AM
U1529A-1R-1-W-I-a	5	9.76	-1.29	61465.58	67.32	3.35	0.927	61429.47	2.68	24.71	5.42	0.71	0.16	March 28, 2024 11:41:38 AM
U1531B-3R-2-W-A-a	3	22.58	1.82	61399.30	70.47	8.07	0.971	61437.19	1.63	28.32	3.31	0.83	0.10	March 28, 2024 2:13:42 PM
U1531B-3R-2-W-A-a	4	10.63	-1.17	61466.03	57.85	3.25	0.936	61435.51	2.02	28.61	4.10	0.83	0.12	March 28, 2024 2:13:42 PM
U1531B-3R-2-W-A-a	5	9.85	-1.61	61459.13	68.04	3.39	0.922	61422.23	2.05	31.99	4.17	0.92	0.12	March 28, 2024 2:13:42 PM
U1529A-1R-1-W-L-b	3	16.02	2.60	61389.67	77.26	7.92	0.957	61428.11	3.45	38.24	6.92	1.12	0.21	March 28, 2024 9:56:07 AM
U1529A-1R-1-W-L-b	4	8.62	-1.08	61458.57	55.92	3.25	0.896	61429.59	3.66	34.83	7.35	1.01	0.22	March 28, 2024 9:56:07 AM
U1529A-1R-1-W-L-b	5	7.48	-1.80	61460.07	72.85	3.34	0.907	61420.85	3.11	33.43	6.27	0.96	0.18	March 28, 2024 9:56:07 AM
U1531B-3R-3-W-M-a	3	26.99	1.65	61403.88	66.34	8.25	0.973	61439.84	2.05	23.60	4.15	0.69	0.12	March 28, 2024 6:23:00 PM
U1531B-3R-3-W-M-a	4	11.55	-1.54	61473.17	64.25	3.20	0.948	61438.30	1.99	23.60	4.04	0.68	0.12	March 28, 2024 6:23:00 PM
U1531B-3R-3-W-M-a	5	10.17	-2.20	61474.19	78.03	3.36	0.946	61433.54	2.37	18.56	4.82	0.54	0.14	March 28, 2024 6:23:00 PM

Table OR4.5. Summary of fitted skewed Gaussian curve parameters, calculated peak positions, $\Delta SK\alpha$ values and calculated S^{6+}/S^{total} values for $SK\alpha$ wavelength scans of silicic melt inclusions. SD = Standard deviation of peak position for 1000 bootstrap samples. See Online Resource 3 for details of curve fitting procedure and uncertainty estimations.

Plots of SK α Wavelength Scans with Skewed Gaussian Fits

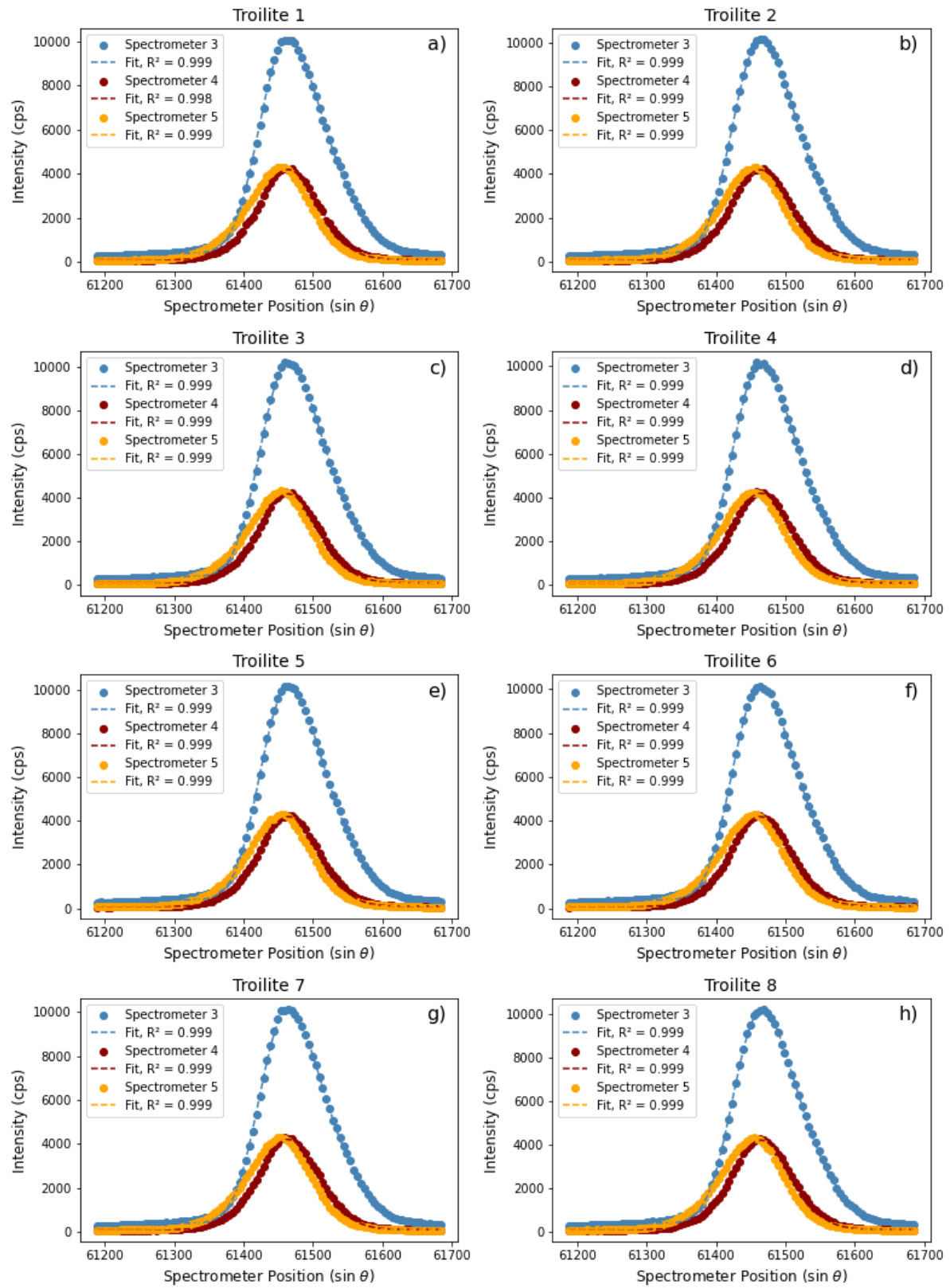


Fig. OR4.1. SK α wavelength scans for troilite with skewed Gaussian fits. Parameters for the fitted curves are in Table OR4.1.

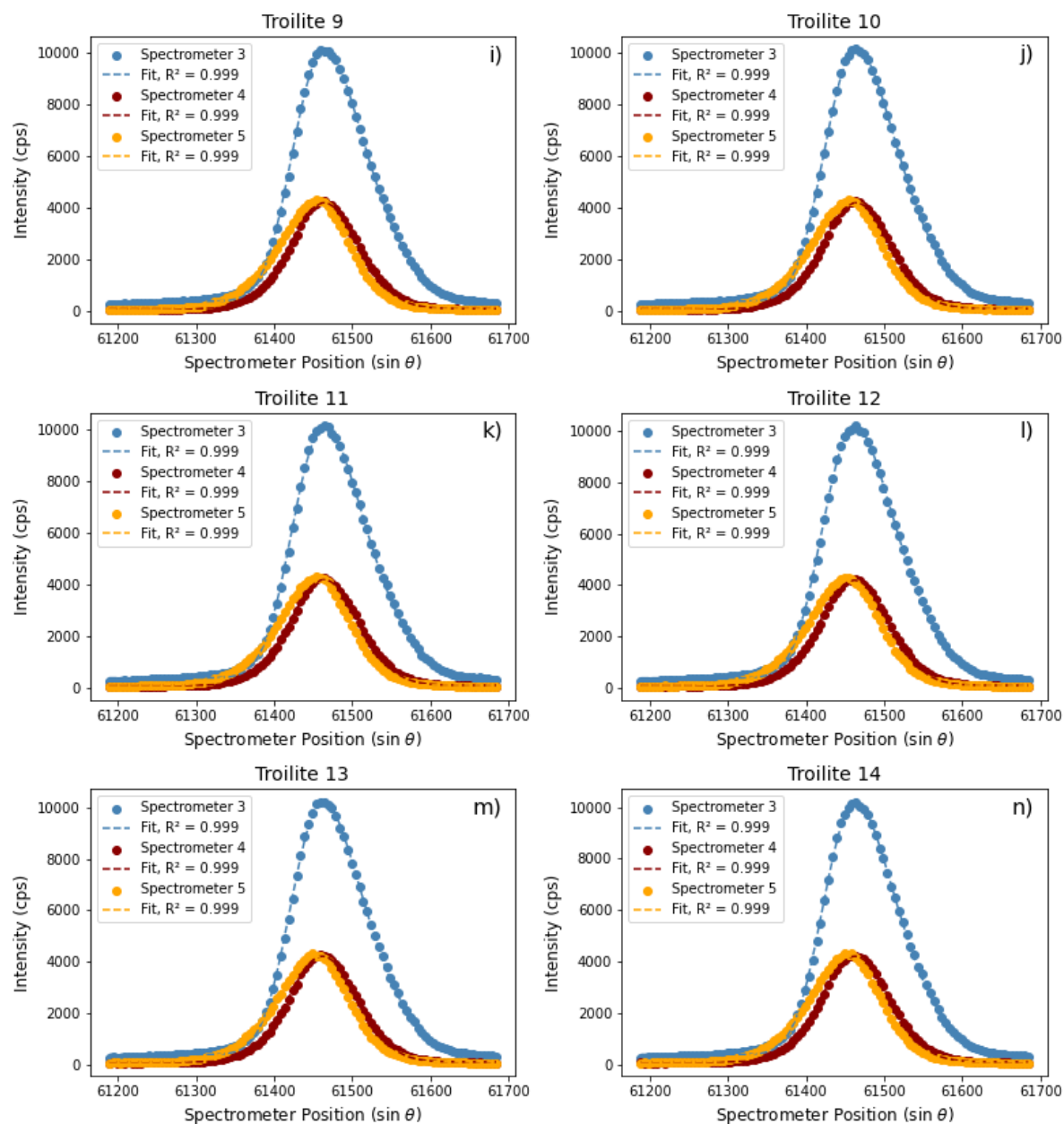


Fig. OR4.1. (Continued)

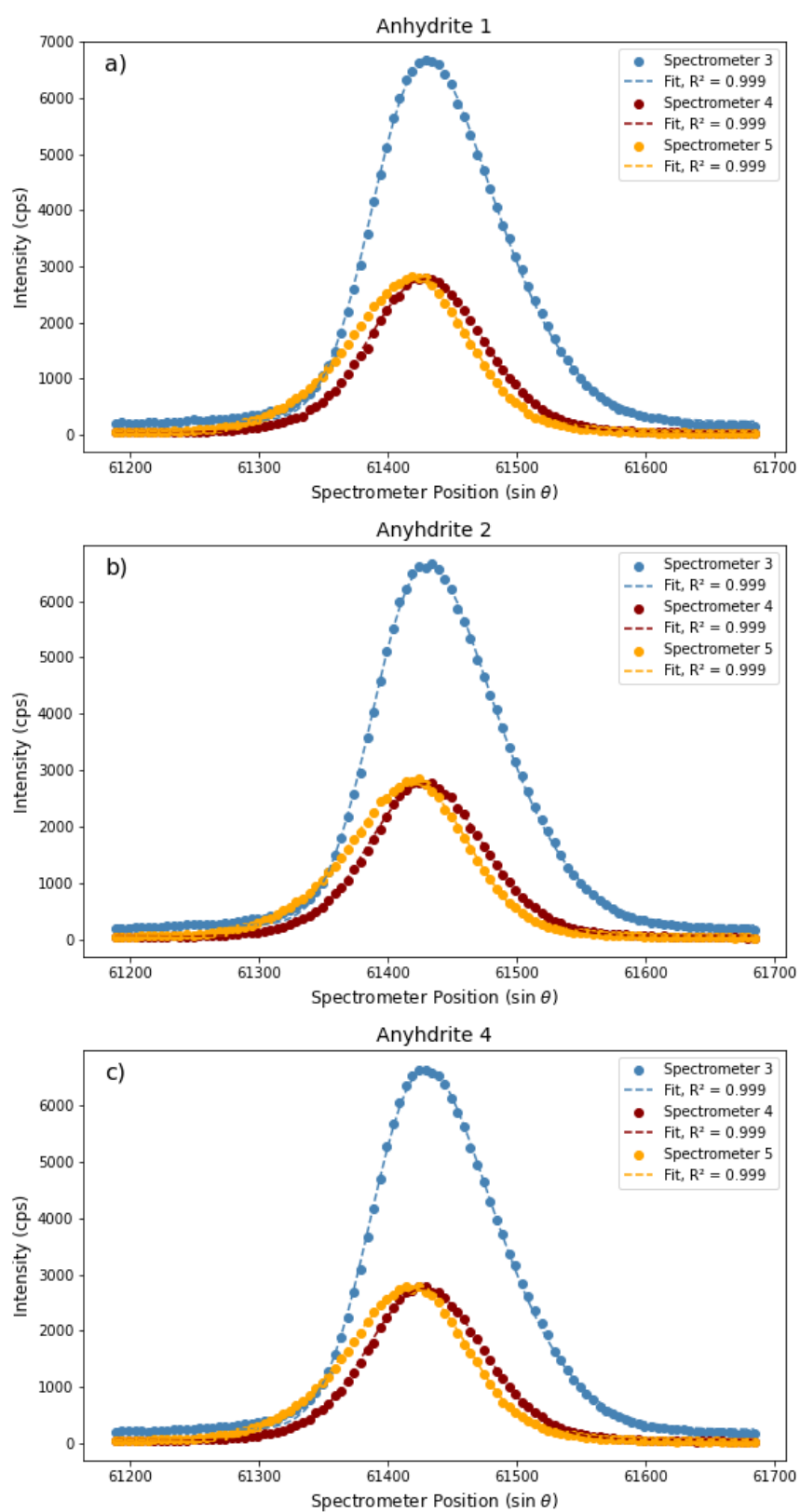


Fig. OR4.2. SK α wavelength scans for anhydrite with skewed Gaussian fits. Parameters for the fitted curves are in Table OR4.2.

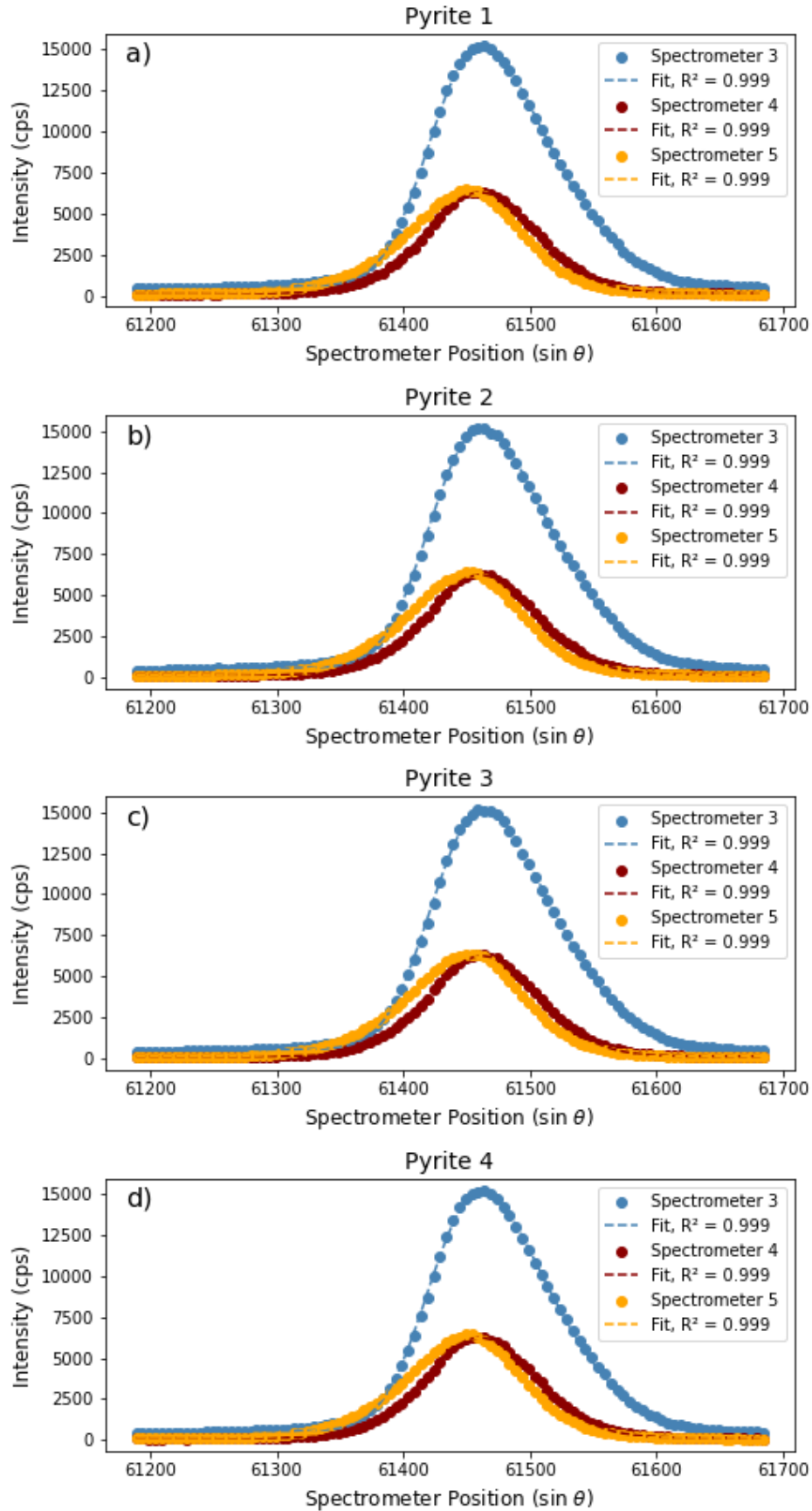


Fig. OR4.3. SK α wavelength scans for pyrite with skewed Gaussian fits. Parameters for the fitted curves are in Table OR4.3.

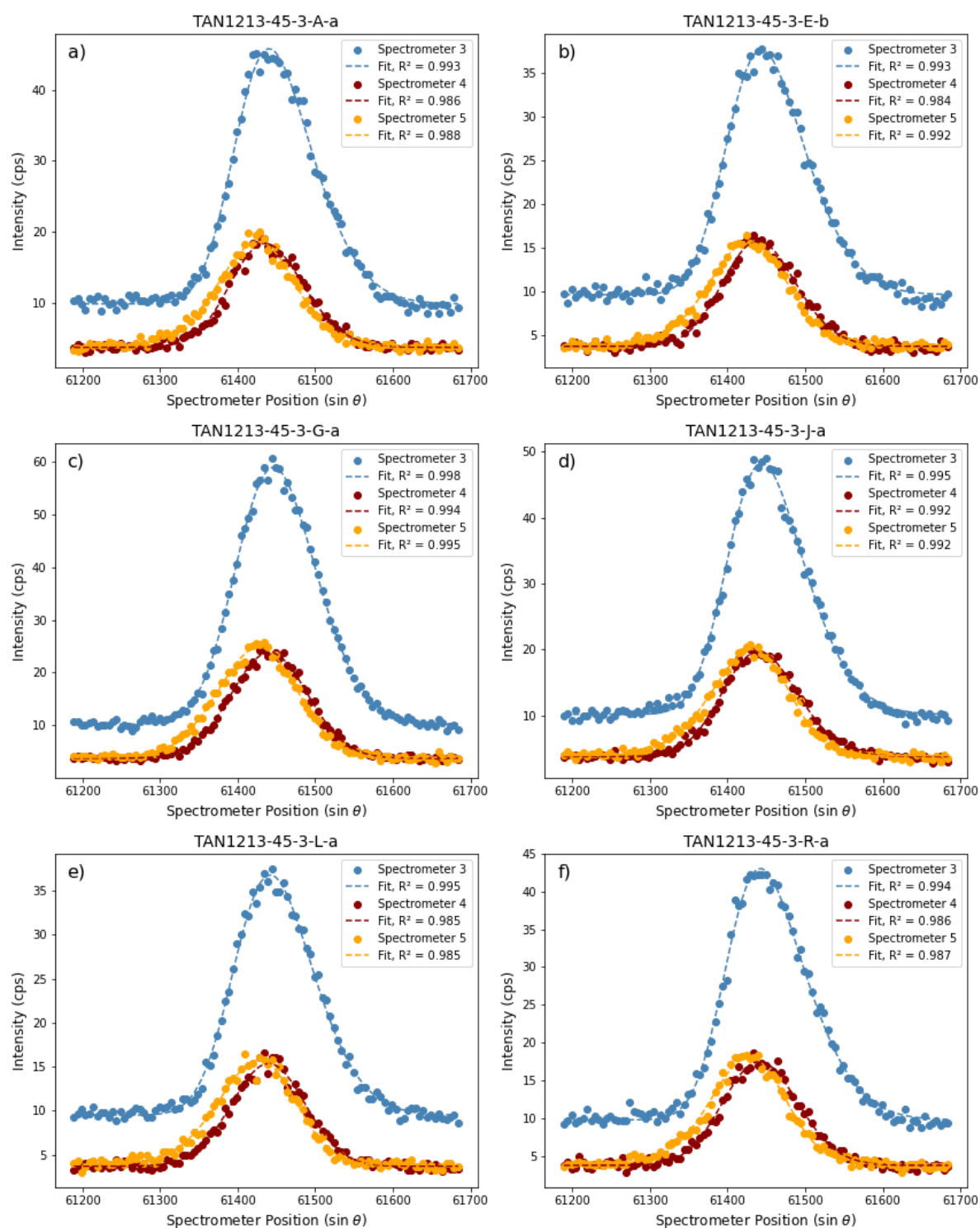


Fig. OR4.4. SK α wavelength scans for basaltic melt inclusions with skewed Gaussian fits. Parameters for the fitted curves are in Table OR4.4.

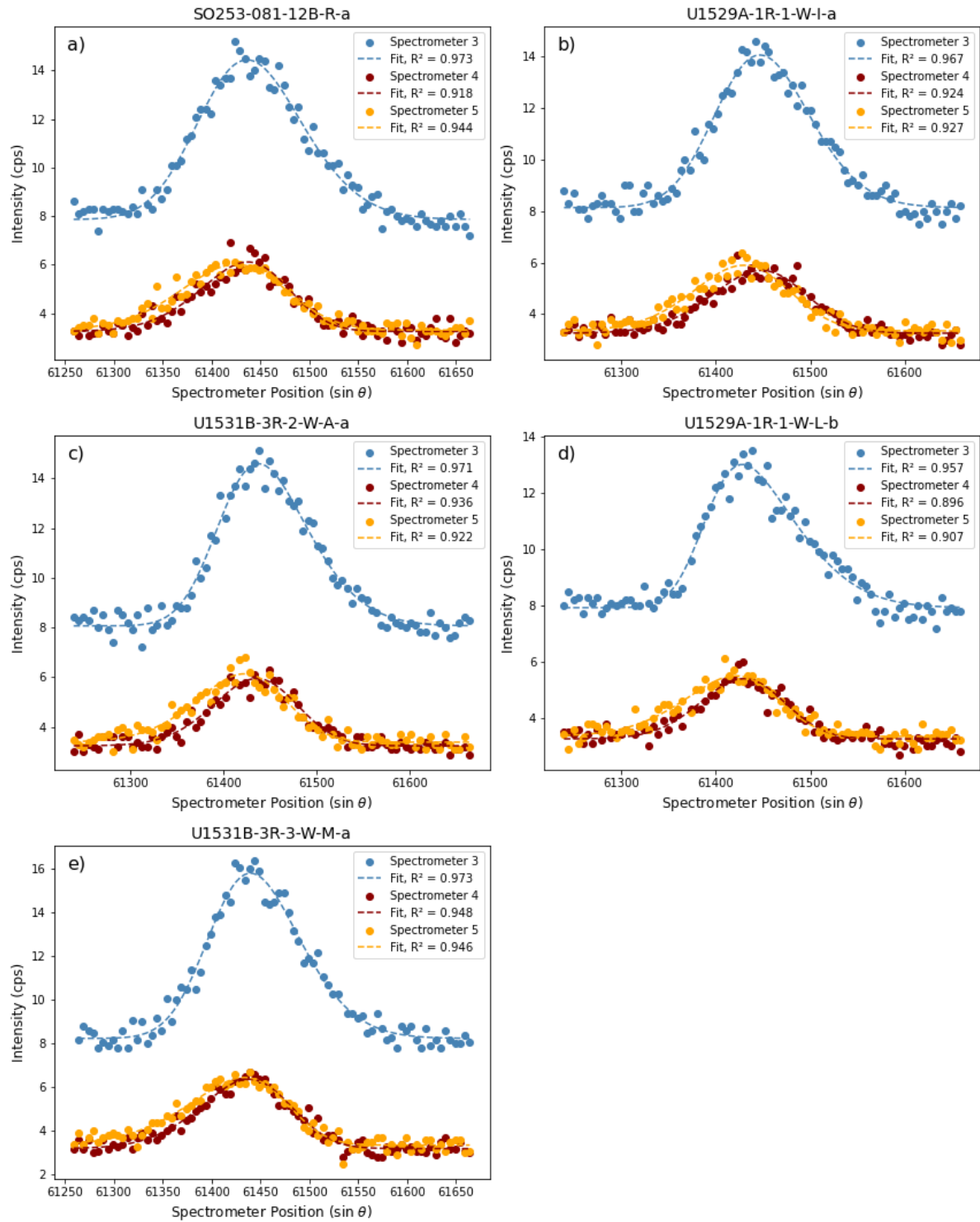


Fig. OR4.5. SK α wavelength scans for silicic melt inclusions with skewed Gaussian fits. Parameters for the fitted curves are in Table OR4.5.