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Analysis of Water Concentration Formed Within Deformed Synthetic Quartz Crystals

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Abstract

Analyzing the strength of synthetic quartz is essential to understanding the strength of natural milky quartz, which likely controls the strength of Earth's continental crust. Synthetic quartz is sometimes used for deformation experiments because it has a homogenous water distribution unlike natural milky quartz. The purpose of this study is to determine if annealing synthetic quartz at T = 600°C will convert the water in synthetic quartz to free water, like milky quartz, but with little water loss. Following two annealing experiments at Texas A&M University, I performed four annealing experiments to measure the water content of five synthetic quartz crystals annealed at T = 600°C for several durations for a total annealing time of 5580000 seconds. Then, I measured the water contents after each annealing experiment. Analyses showed that the water loss was very small (~10%), but the water still resembled gel-type water of synthetic quartz, rather than free water in inclusions similar to that found in natural milky quartz.

Introduction

Quartz is an abundant mineral throughout Earth's continental crust, and because of this abundance, its strength likely controls the strength and response of the mid to lower continental crust after earthquakes (Burgmann and Dresen, 2008). Natural quartz is weak relative to other minerals in the continental crust (Hacker et al., 1990; Stipp et al., 2002). The cause of this weakness is the presence of water in fluid inclusions, which weaken silicon-oxygen (Si-O) bonds in natural milky quartz (Griggs 1967). Natural milky quartz lacks homogeneous distribution of water inclusions, which can cause heterogeneous strain during deformation. Consequently, milky quartz is not a good material for experimental investigations of quartz strength because the strain distribution will be heterogeneous if the water content is also heterogeneous (Kekulawala et al.,

1978; Kronenberg et al., 2001; Holyoke and Kronenberg, 2013; and Stünitz et al., 2017). To avoid that complication, synthetic quartz is sometimes used in experimental studies because the water distribution is much more homogeneous (Kekulawala et al., 1978; Griggs et al., 1966; Poston, 2017). However, the water in synthetic quartz is not the same as that in natural milky quartz (Figure 1). Water in synthetic quartz is included as gel-like (non-freezable) defects in the quartz structure, not inclusions of free water like in natural milky quartz. Experimentalists convert the water in synthetic crystals to free water inclusions by annealing the crystals at high temperatures (T = 900°C), but this annealing can cause major water loss (> 50%). The main goal of this project is to determine if I can convert the water in synthetic quartz to the same free water observed in milky quartz without significant water loss by annealing crystals of quartz at a lower temperature (T = 600°C).

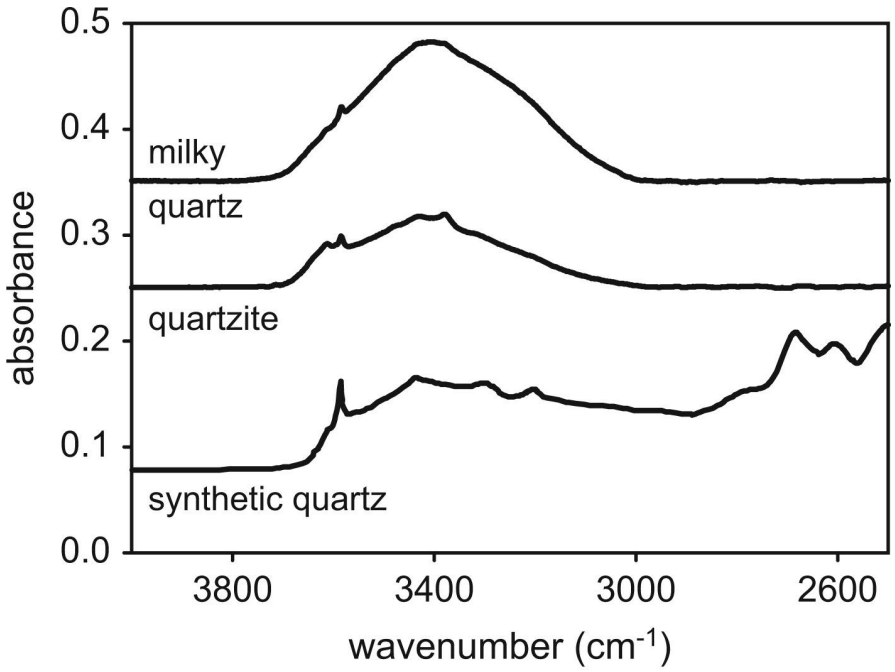


Figure 1. (top) IR spectra for deformed Arkansas milky quartz single crystal (Holyoke and Kronenberg, 2013).

Methods

In order to determine how water content and type in synthetic crystals changed as a function of annealing time, I annealed cores from synthetic quartz crystals at T = 600°C for t_{total} = 198000, 558000, 1980000, and 5580000 seconds (Table 1) and analyzed the water content after each annealing using a Fourier Transform Infrared Spectrometer (FTIR).

Table 1. Summary of anneal step times and total anneal times.

Anneal	Location	t_{step} (s)	t_{total} (s)
1	Texas A&M	1.44E+04	1.98E+04
2	Texas A&M	3.60E+04	5.58E+04
3	Univ. of Akron	1.42E+05	1.98E+05
4	Univ. of Akron	3.60E+05	5.58E+05
5	Univ. of Akron	1.42E+06	1.98E+06
6	Univ. of Akron	3.60E+06	5.58E+06

The cores were provided by Dr. Andreas Kronenberg of Texas A&M University, who started the study by performing two annealing experiments at 600°C for t_{total} = 19800 seconds and 55800 seconds. Prior to my first annealing experiment, I collected FTIR spectra from cores and on a natural Brazil quartz crystal (Figure 2) to duplicate the most recent analysis performed at Texas A&M University.

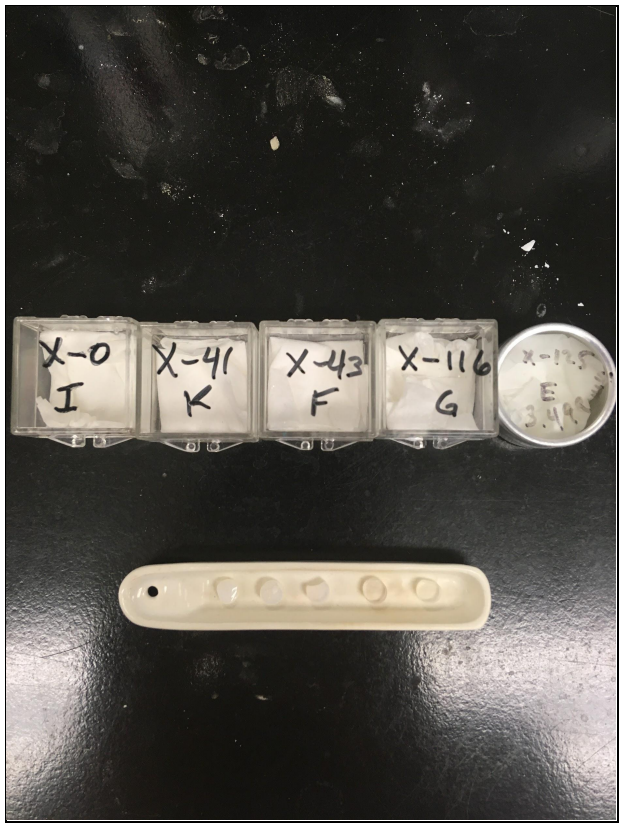


Figure 2. The five synthetic quartz crystal cores placed on a slide before undergoing heat treatment at the University of Akron. The order of the crystals (from left to right) aligns with the cases placed above the slide.

I used the Thermo-Nicolet 860 FTIR at the National Center for Education and Research on Corrosion and Materials Performance (NCERCAMP) at The University of Akron to measure the water content of each core individually. The FTIR device transmits a light beam through the sample, which selectively absorbs light at specific wavelengths due to chemical bond vibration energy. Free water forms a broad absorbance band from 3000-3650 cm^{-1} (Figure 1), CO_2 forms two peaks near 2300 cm^{-1}, and Si-O bonds form peaks in the 1000-2000 cm^{-1} range. The water in synthetic quartz forms a broad bond of absorbance from 2400-3650 cm^{-1} (Figure 1), but Si-O bonds in synthetic quartz are identical to natural quartz. All spectra were normalized to 1cm

thicknesses by dividing the absorbance by the thickness of the core in centimeters. I subtracted a dry quartz spectra from these normalized spectra to remove any Si-O overtones from the water region (Figure 3). After this process, I measured the integrated absorbance by measuring the area beneath the spectra from 2400-3650 cm^{-1}. This integrated area was used to calculate the water content using the calibration of Aines et al. (1984).

$$\text{Concentration H}/10^6\ \text{Si (ppm)} = 1.05 * \Delta(cm^{-2}) \qquad \text{(Eq 1)}$$

where $\Delta = \int$ absorbance from 3750 cm^{-1} to 2400 cm^{-1}, suitably corrected for background Si-O absorptions

The cores were annealed using the tube furnace in the geochemistry lab. I annealed the cores for t_{total} = 198000, 558000, 1980000, and 5580000 seconds at 600°C in order to convert the defect-water to free-water inclusions in the five quartz crystals. The annealing was conducted at 600°C to avoid water loss, which occurs at higher temperatures (900°C; Poston, 2017). The five cores were placed in the center of the furnace, where the temperature gradient is low (< 10°C). After each annealing experiment, the water content was measured before starting the subsequent annealing experiment.

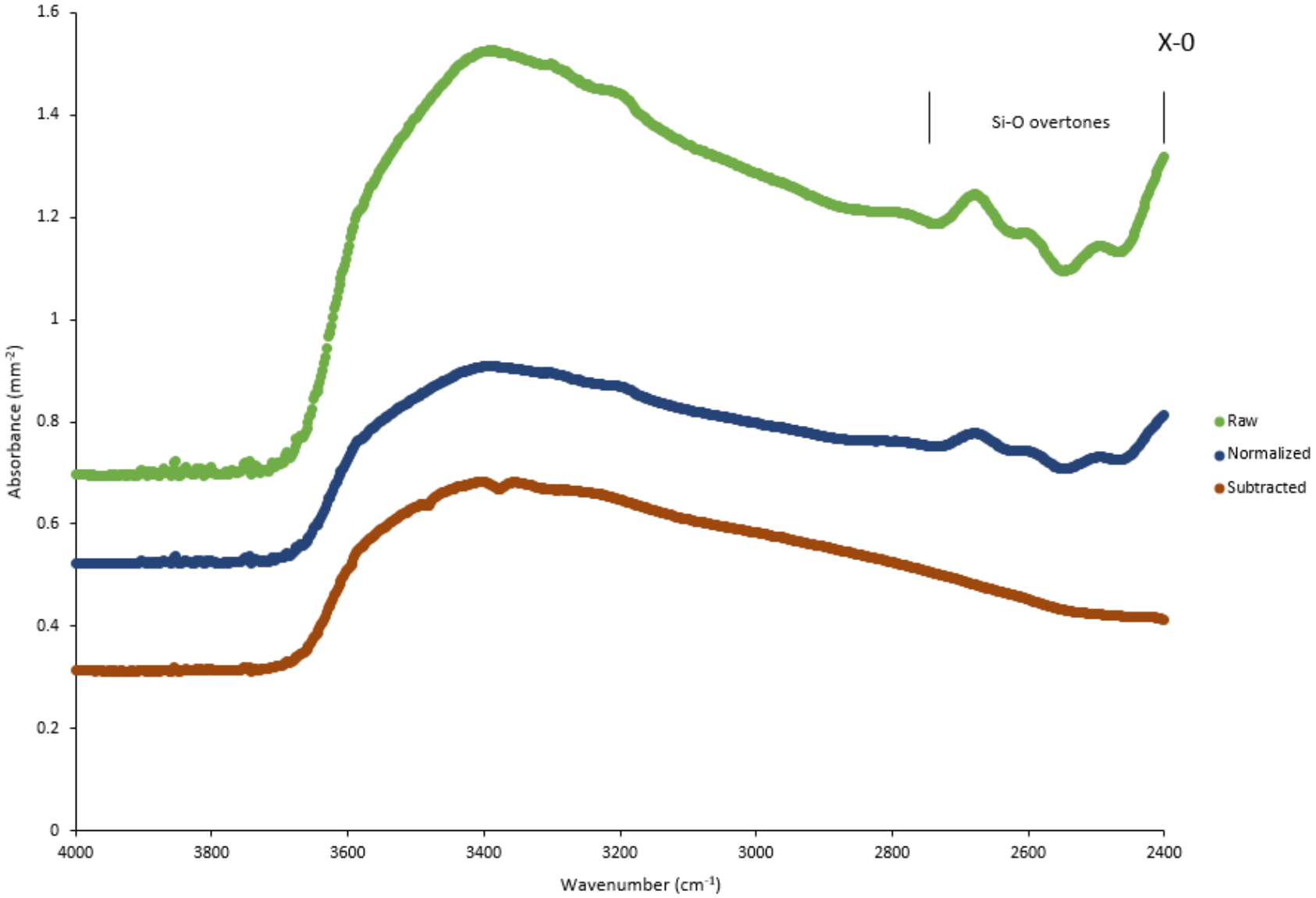


Figure 3. Water absorbance spectra of crystal X-0 for the raw, normalized, and subtracted values after 5580000 seconds of annealing.

Results

Spectra were measured after two annealing events at Texas A&M University and four annealing events at The University of Akron. Crystal X-41 had the greatest starting water content (an outlier value of 5791 H/10^6 Si) while crystal X-116 had the lowest starting water content (79 H/10^6 Si) and crystals X-0, X-43, and X-125 had individual water contents starting at 2745, 1504, and 1063 H/10^6 Si (Table 2). Water contents for all crystals decreased slightly throughout the annealing process (Figure 4). However, the form of the water spectra did not change from gel-type water to free water, even after 5580000 seconds of annealing (Figures 5, 6, 7, 8, and 9).

The spectra for crystals X-0, X-41, X-43, and X-125 all had peaks at roughly 3600 cm^{-1} and valleys at 3400 and 3500 cm^{-1} (Figures 5, 6, 7, and 9) whereas crystal X-116 had a relatively flat spectra, which gradually increased after 3400 cm^{-1} (Figure 8). The spectra for crystal X-0 at 0 sec had a significant bump around 3000 cm^{-1}, which vanished by the 19800 sec spectra (Figure 5). The spectra for crystal X-41 at 0 sec had a significant peak at 3400 cm^{-1}, where the size decreased over time (Figure 6). The spectra for crystal X-43 were consistent from 3300 cm^{-1} to 2400 cm^{-1} (Figure 7). The spectra for crystal X-125 after 3400 cm^{-1} transitions from arch-shaped to slump-shaped, with other smaller peak and valley variations from 2400-2700 cm^{-1} (Figure 9).

Table 2. Experimental data for the five synthetic quartz crystal samples. The time (s) represents the annealing process duration.

Sample #	FTIR Location	Time (s)	Absorbance (cm^{-2})	Water Content ($H/10^6$ Si)
X-0	Texas A&M	1.00E+00	2614	2745
	Texas A&M	1.98E+04	2552	2680
	Texas A&M	5.58E+04	2566	2694
	Univ. of Akron	5.58E+04	2329	2445
	Univ. of Akron	1.98E+05	2477	2601
	Univ. of Akron	5.58E+05	2380	2499
	Univ. of Akron	1.98E+06	2375	2494
	Univ. of Akron	5.58E+06	2360	2479
X-41	Texas A&M	1.00E+00	5515	5791
	Texas A&M	1.98E+04	2291	2406
	Texas A&M	5.58E+04	2142	2249
	Univ. of Akron	5.58E+04	1692	1777
	Univ. of Akron	1.98E+05	1473	1547
	Univ. of Akron	5.58E+05	1565	1643
	Univ. of Akron	1.98E+06	1783	1872
	Univ. of Akron	5.58E+06	1623	1705
X-43	Texas A&M	1.00E+00	1432	1504
	Texas A&M	1.98E+04	1417	1488
	Texas A&M	5.58E+04	1365	1433
	Univ. of Akron	5.58E+04	1349	1416
	Univ. of Akron	1.98E+05	1301	1366
	Univ. of Akron	5.58E+05	1249	1312
	Univ. of Akron	1.98E+06	1318	1384
	Univ. of Akron	5.58E+06	1259	1322
X-116	Texas A&M	1.00E+00	75	79
	Texas A&M	1.98E+04	191	201
	Texas A&M	5.58E+04	193	203
	Univ. of Akron	5.58E+04	116	121
	Univ. of Akron	1.98E+05	72	76
	Univ. of Akron	5.58E+05	89	94
	Univ. of Akron	1.98E+06	42	45
	Univ. of Akron	5.58E+06	-	-
X-125	Texas A&M	1.00E+00	1012	1063
	Texas A&M	1.98E+04	910	956
	Texas A&M	5.58E+04	997	1047
	Univ. of Akron	5.58E+04	846	889
	Univ. of Akron	1.98E+05	762	800
	Univ. of Akron	5.58E+05	859	902
	Univ. of Akron	1.98E+06	854	897
	Univ. of Akron	5.58E+06	626	657

*The table provides the time 5.58E+04 s twice due to one measurement being taken at Texas A&M University after the second heat treatment and once at the University of Akron before the third heat treatment.

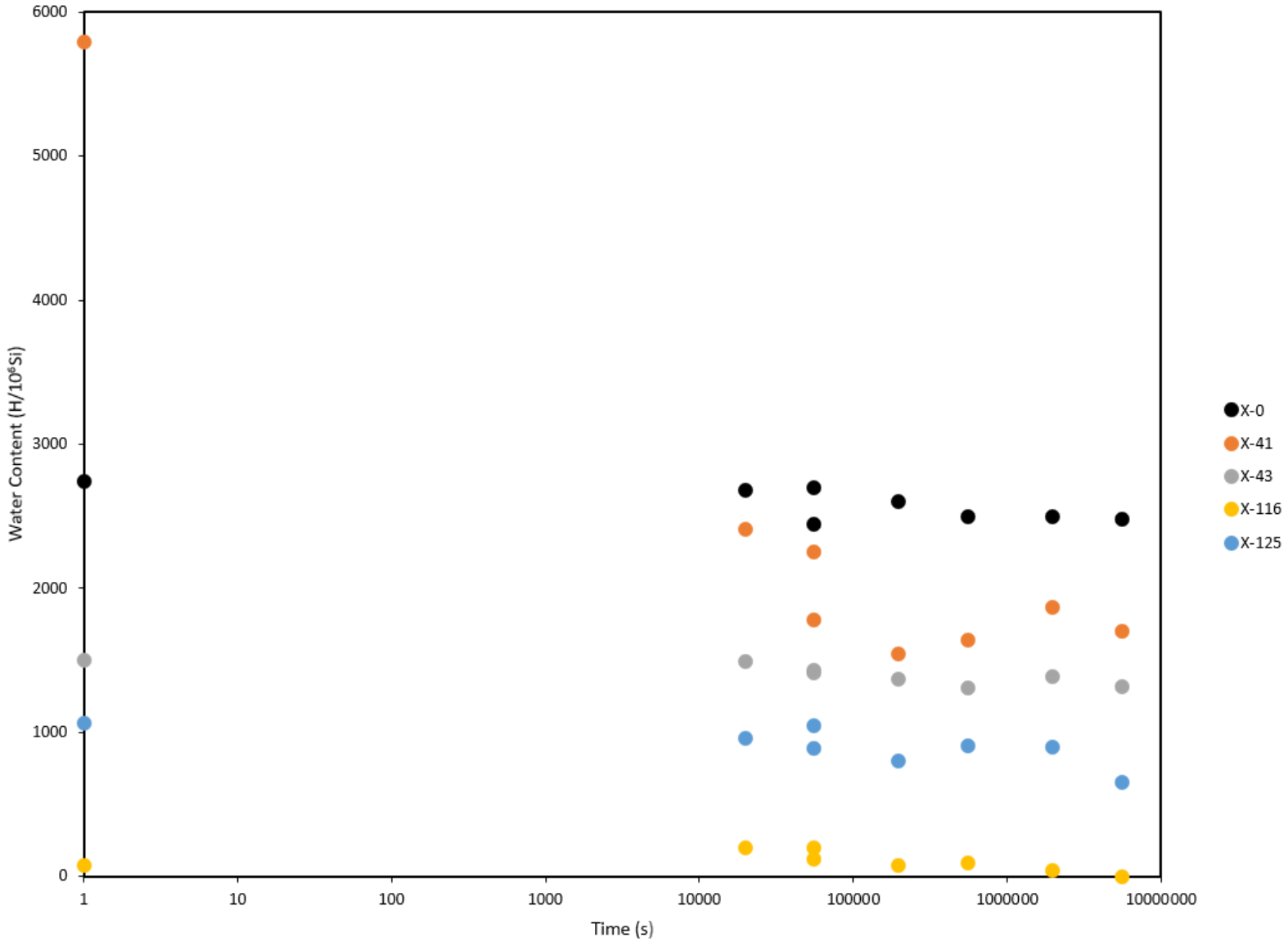


Figure 4. Water content data for all five synthetic quartz crystal samples as calculated by using the FTIR data.

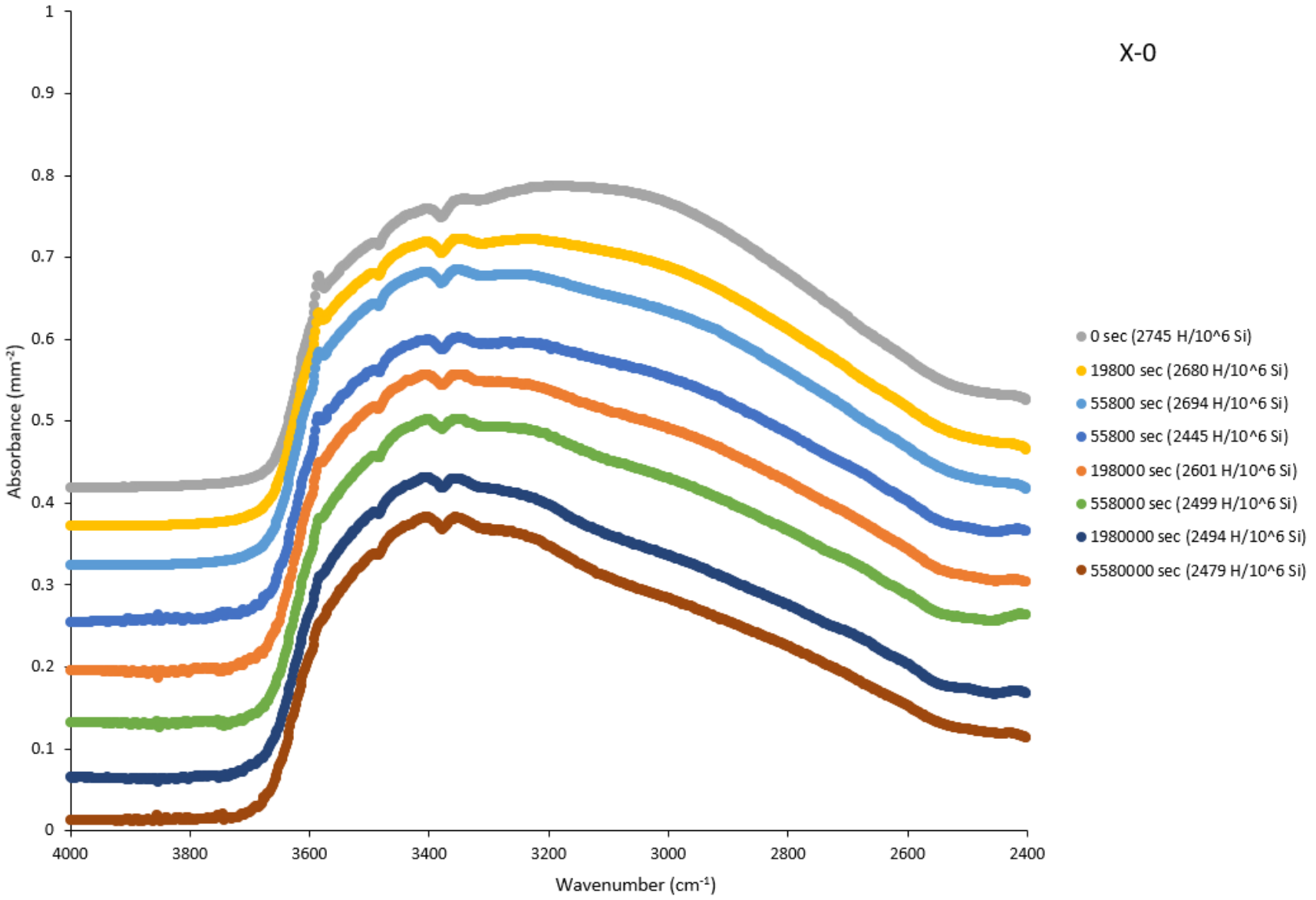


Figure 5. Water absorbance spectra over the annealing process timeline of crystal X-0.

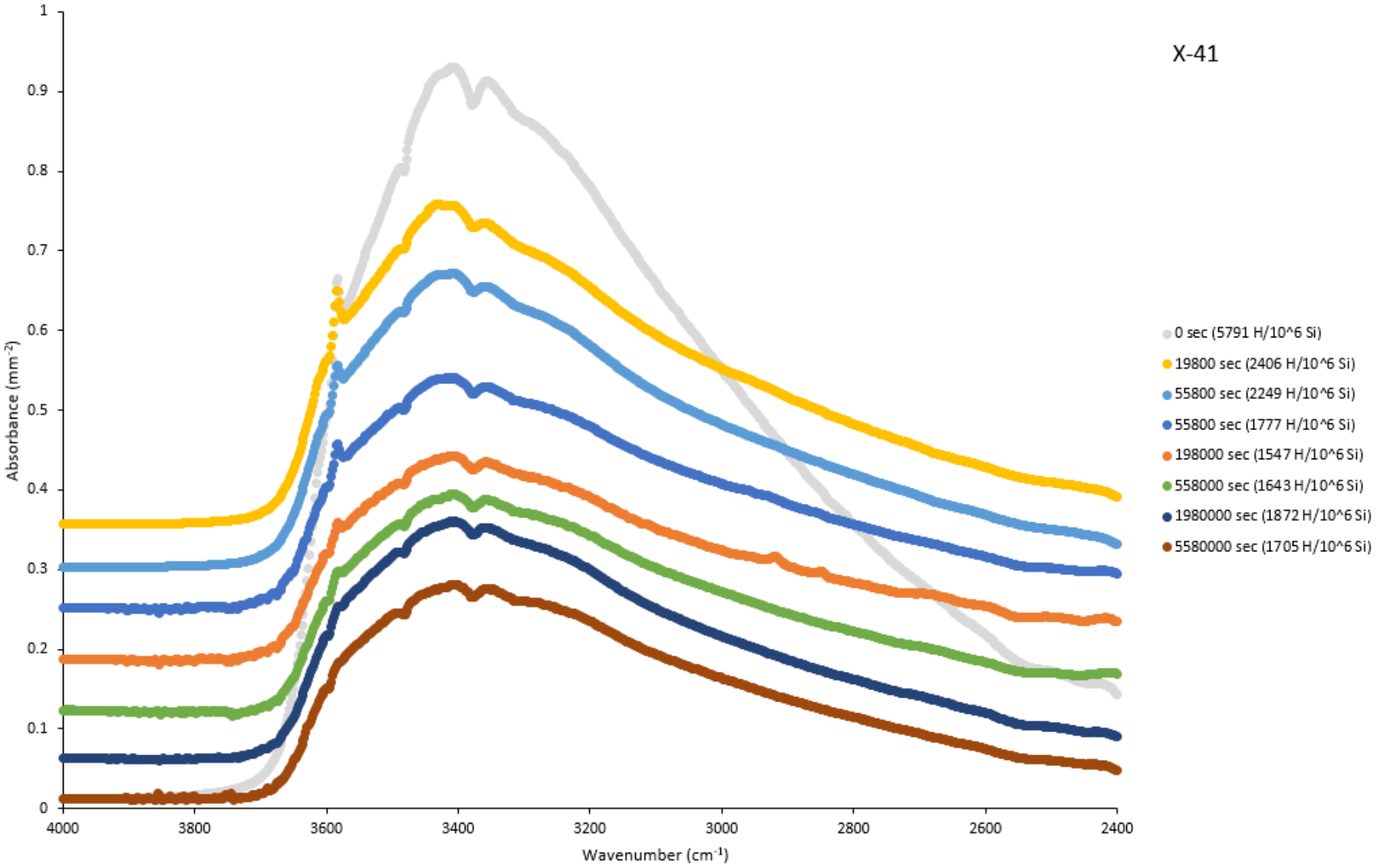


Figure 6. Water absorbance spectra over the annealing process timeline of crystal X-41. The spectra for t = 0 sec was adjusted to fit the scale.

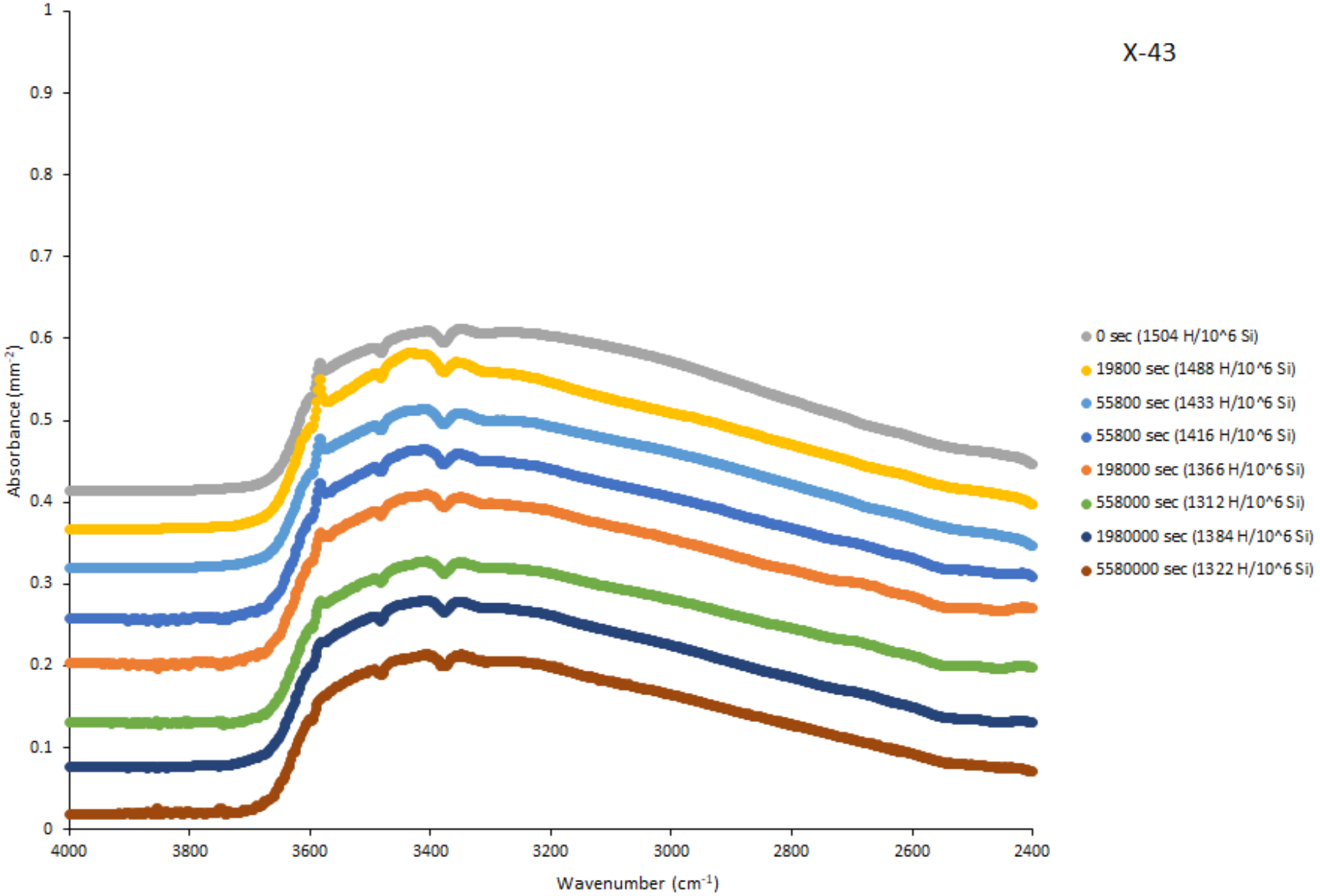
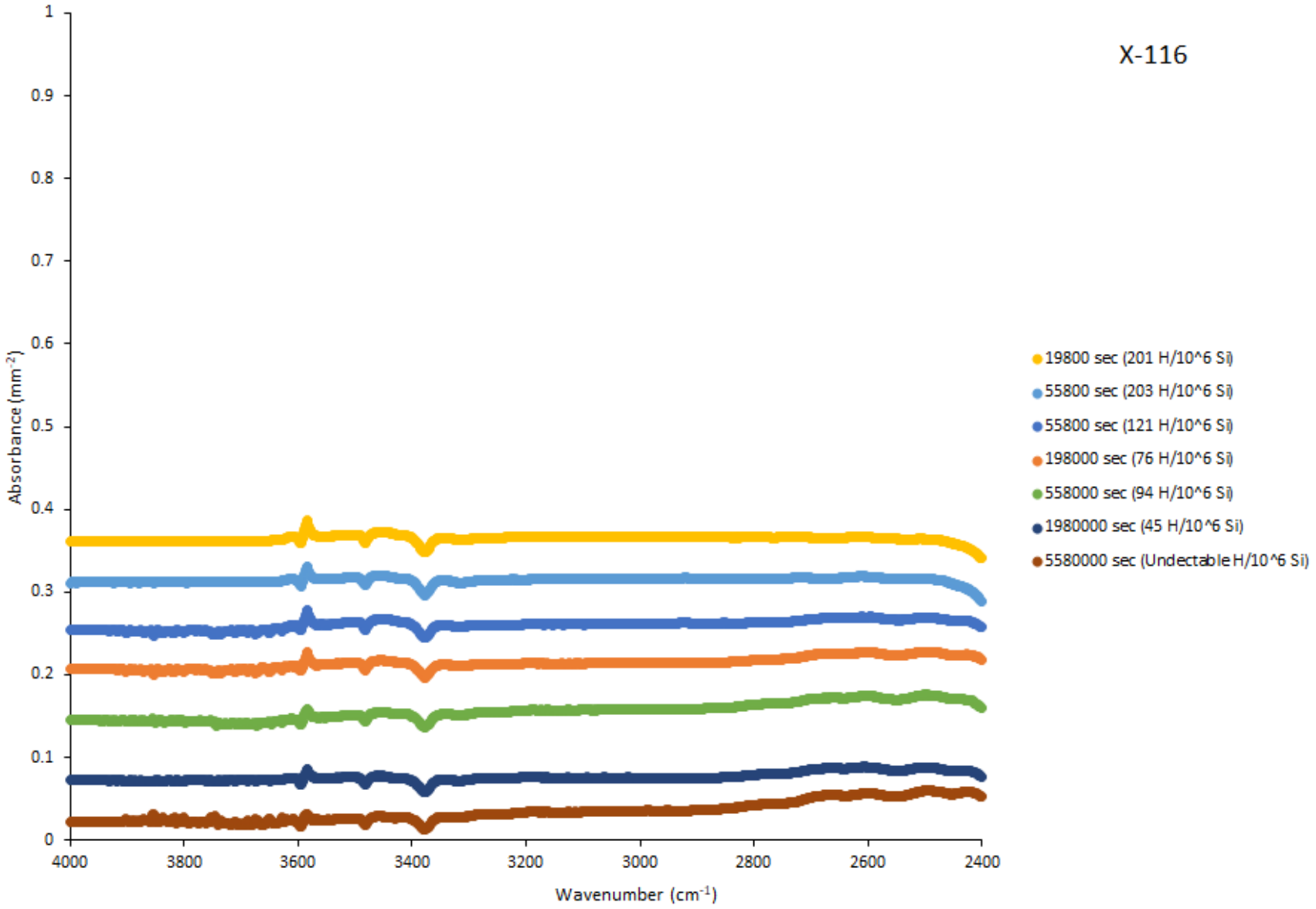


Figure 7. Water absorbance spectra over the annealing process timeline of crystal X-43.



.**Figure 8.** Water absorbance spectra over the annealing process timeline of crystal X-116.

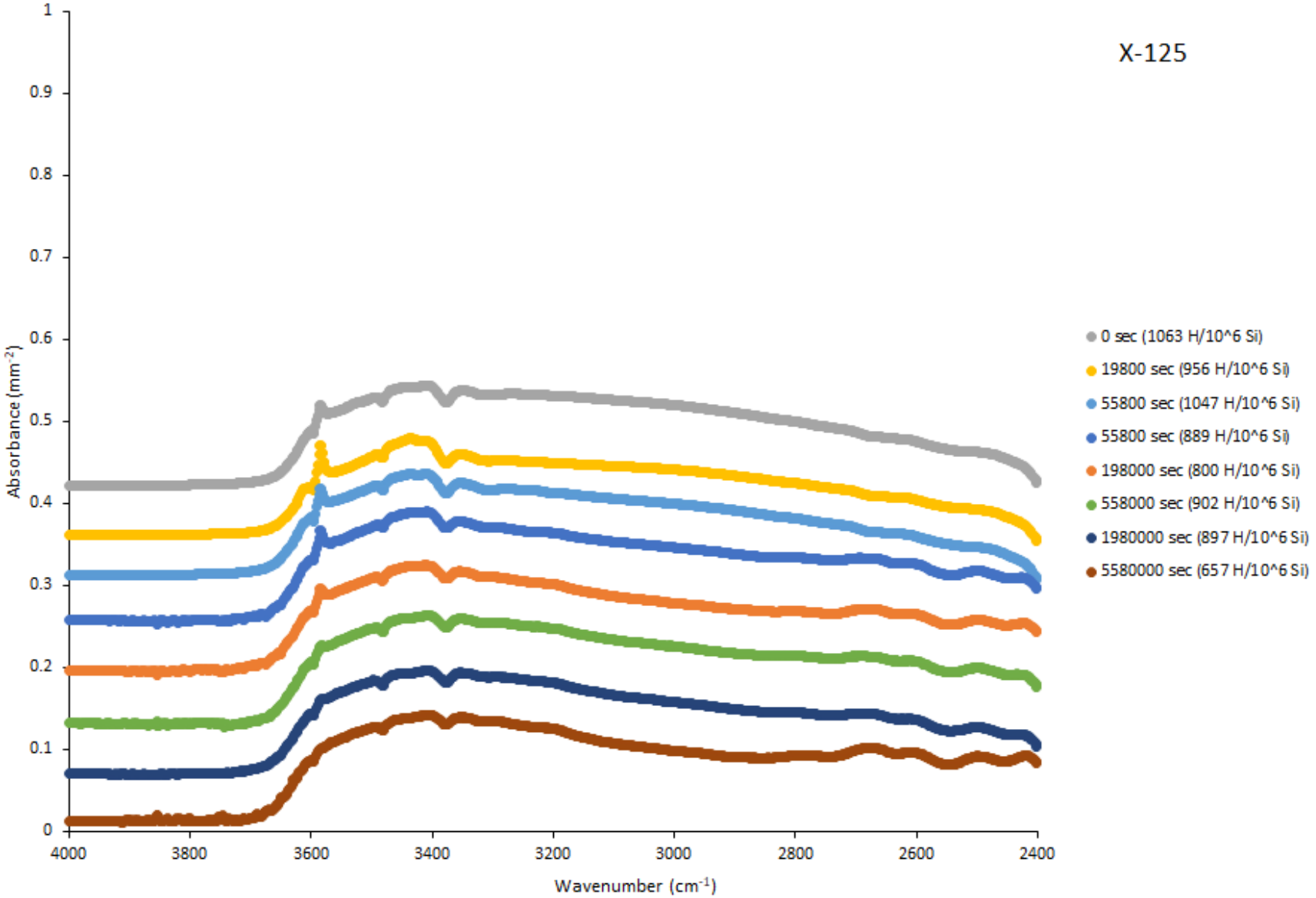


Figure 9. Water absorbance spectra over the annealing process timeline of crystal X-125.

Discussion

The main objective for this experiment was to determine if the water in synthetic quartz crystals could be converted from the homogeneous distribution at gel-type water to free water in inclusions, similar to natural milky quartz, without significant water loss. The hypothesized conversion could be determined by observing the absorbance spectra among the different synthetic quartz cores. The spectra of natural milky quartz, which has free water present in fluid inclusions, has an absorbance bond from 3000-3750 cm^{-1}, with a peak at 3400 cm^{-1} (Figure 1). The spectra of synthetic quartz, which has a gel-type water, has an absorbance band from 2400-3750 cm^{-1}, with various peaks and valleys (Figures 1, 5, 6, 7, 8, and 9).

The absorbance spectra for all five cores have an absorbance band consistent with gel-type water and not inclusions of free water similar to natural milky quartz. Thus, no conversion occurred during this experiment, despite annealing the crystals at a lower temperature of 600°C for 5580000 seconds (Figure 4). However, all five crystals display slightly lower water content values following the last round of heat treatment, but not as great as the experiments by Poston (2017) and Kekulawala et al. (1978) where more water loss occurred due to annealing at 900°C. Yet, the experiments by Poston (2017) and Kekulawala et al. (1978) had a more successful water conversion. These results indicate that temperatures > 600°C are necessary to convert gel-type water to free water and it may be impossible to avoid water loss entirely.

Conclusion

It is imperative to understand the strength of natural milky quartz, which is an abundant mineral in Earth's continental crust. The homogeneous distribution of water in synthetic quartz makes it desirable for experimental use, but problematic because of the difference between the water types in synthetic and milky quartz. I performed four annealing experiments to determine if the gel-type water of synthetic quartz could be converted to free water in inclusions, such as that of natural milky quartz, while at a lower temperature of 600°C. The water content of each crystal sample was measured using the Thermo-Nicolet 860 FTIR. No conversion of the water from gel-type to free water occurred. However, there was minimal water loss, which happens at higher temperatures, due to annealing at a lower temperature. The spectra of the synthetic quartz crystals shared a similar trend, with peaks at roughly 3600 cm^{-1} and valleys at 3400 and 3500 cm^{-1}, with the exception of crystal X-116 since it was a much drier sample.

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