Silicon Detectability in Corundum Using LA-ICP-QMS (Laser Ablation–Inductively Coupled Plasma–Quadrupole Mass Spectrometry)

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Rubies and sapphires are varieties of the mineral corundum, which has a bulk composition of Al_2O_3. Pure alumina is colorless, so the colors of rubies and sapphires come from various trace elements in the corundum lattice: Cr in rubies, Fe and Ti in blue sapphires and Mg in yellow sapphires. However, there are trace elements that do not produce visible color, but affect the stone's apparent color in other ways. Emmett et al. (2003) presented details about the coloring in gem corundum. Among all trace elements, silicon occupies a special position because of its quadvalence (4+ charge) and its abundance in the earth's crust and mantle. Emmett et al. (2003) demonstrated that the difference between [Mg^{2+} + Be^{2+}] and [Ti^{4+} + Si^{4+}] concentrations directly affects the resulting color in a beryllium-diffused sapphire. Among these four elements, the other three (Mg, Be and Ti) are readily measurable; thus it is important to analyze silicon detectability.

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) has gained prevalence among gemological laboratories. Its primary task is detecting beryllium in suspected diffused corundum. Nevertheless, the instrument is capable of analyzing the vast majority of elements in the periodic table, and it is no surprise that gem laboratories are using the technique to determine concentrations of many other elements in mineral varieties. The most popular ICP-MS systems are quadrupole-based and therefore will be shorthanded as LA-ICP-QMS. So the question becomes: Is it possible to detect Si in corundum using LA-ICP-QMS? If so, what is the detection limit of Si?

Silicon has three natural isotopes: ^{28}Si (m = 27.97692 amu; atomic mass unit, a measure of mass in atomic scale, see IUPAC [1996]), ^{29}Si (m = 28.97649 amu), and ^{30}Si (m = 29.97377 amu). When analyzing corundum using LA-ICP-QMS, the Si isotopes always have high background interference from Si in the environment (such as the quartz torch or particulates in the air) and polyatomic interferences from the environment such as $^{14}N^{14}N^{+}$ (m = 28.00615 amu), $^{14}N^{15}N^{+}$ (m = 29.00318 amu), or $^{14}N^{16}O^{+}$ (m = 29.99799 amu). The most definitive way to distinguish Si from any interference is through a high-resolution mass spectrometer. However, ICP-QMS systems do not have sufficient resolution to resolve these interferences; only a magnetic-sector-based instrument does.

During laser ablation of a corundum sample, aluminum and additional oxygen from corundum matrix and other elements in the plasma may react and form additional ions that interfere with Si signal, such as $^{27}Al^{1}H^{+}$ (m = 27.98936 amu) or $^{27}Al^{2}H^{+}$ (m = 28.99564 amu). The first step to establishing Si detectability is knowing if any such additional interference exists. If so, it must be separated or accounted for. The key to this problem lies in samples. In analytical chemistry, every experiment should have a blank sample. This special sample has the same matrix material without any of the interested analytes. In the case of corundum analysis, this

“true blank” sample ideally should be pure corundum with no trace elements. Often, though, a gas blank is used instead of the “true blank” because it is very difficult to acquire such high purity with corundum. The gas blank is a run with no laser firing—only the carrier gas is on. Typical colorless synthetic sapphire is 99.5%–99.9% alumina. For a “true blank” sample in chemical analysis, the impurity level should be much lower than 1000 ppmw (ideally 0; a workable value should be at least a factor of ten less than the lowest concentration one wants to measure). Careful LA-ICP-QMS experimentation on ultra-high-purity corundum samples is the first step to answering the problem of additional interference.

Ultra-high-purity sapphire samples from Crystal Systems, Inc. were obtained by Dr. John Emmett, who kindly donated three discs for this study. Crystal Systems grows its sapphire crystals using HEM (Heat Exchanger Method). The starting material of these three samples was scrap from previous high-purity-growth runs. Recrystallization is the best process for purifying a crystal. These crystals were recrystallized a few times and thus were believed to have less than 1 ppmw impurity. These discs were 13–14 mm in diameter, 2–3.5 mm thick and were doubly polished down to 50,000-mesh (1/2 micron) diamond slurry. They were then ultrasonically cleaned in 2% Alconox solution for 1 hour and then soaked in aqua regia for 18 hours to clean off any residue from the cutting and polishing process. Next, they were cleaned in distilled water and wiped dry using KimWipes. They were then wrapped in clean KimWipes for storage. Handling of these crystals is always done by hand, wearing latex gloves, and no metal or human skin ever touches the surface.

Chemical analysis was performed using a Thermo X-series II ICP-QMS with a New Wave Research UP-213 laser ablation unit. The UP-213 utilizes a frequency-quintupled Nd:YAG laser to produce 213 nm wavelength emissions with 4 nanosecond pulse width. The laser parameters are 55 micrometer diameter spot, 15 Hz repetition rate and 10–11 J/cm^2 fluence. The ablated materials were carried by helium gas to the mass spectrometer in an aerosol form. The ICP-QMS was operated at 1200 W forward power and tuned to maximize Be counts while ablating NIST 612 glass. The tuning sequence also controlled the ThO/Th ratio within 2% (the typical value is ~ 1.7 %).

The first experiment was a mass scan, from 4.5 to 250, with 0.1 amu resolution. The laser was set to a line raster mode with the abovementioned parameters. The raster line was 1500 micrometers long and the raster speed is 15 micrometers/second, for a total ablation time of 100 seconds. In all, 60 scans were averaged within the ablation time. We also collected a gas blank scan to compare the difference. The gas blank run involved exactly the same samples and He carrier gas running at the same flow rate (760 ml/min), but without laser ablation. Comparing the results between the gas blank and the ultra-high-purity corundum ablation runs told us what signal actually comes from ablation aerosol.

The results are summarized in figure 1. The trace displayed in figure 1 shows a scan of 24 to 35. The blue trace is the gas blank, and the red trace is the scan result from the ablation of ultra-pure sapphire. Only the pulse-counting mode signals are shown (Most modern commercial ICP-QMS systems are equipped with an electron multiplier that can be operated in a pulse-counting mode for low concentrations and an analog mode for high concentrations). The blue trace can be considered the background of the system when the laser is not firing. The discrepancy between these two traces at mass number 29 indicated some ions with that

mass number were present in the aerosol from the laser ablation. In addition to 29, similar discrepancies showed in mass numbers 31, 33, and 34 corresponded to ^{31}P, ^{33}S and ^{34}S, indicating some ions with these mass numbers were also present in the plasma. These signals could be due to other interferences as well, but that is not the focus of this study. The ^{28}Si signal had a similar discrepancy (increased counts; see figure 3), but it is not shown in figure 1 due to scaling.

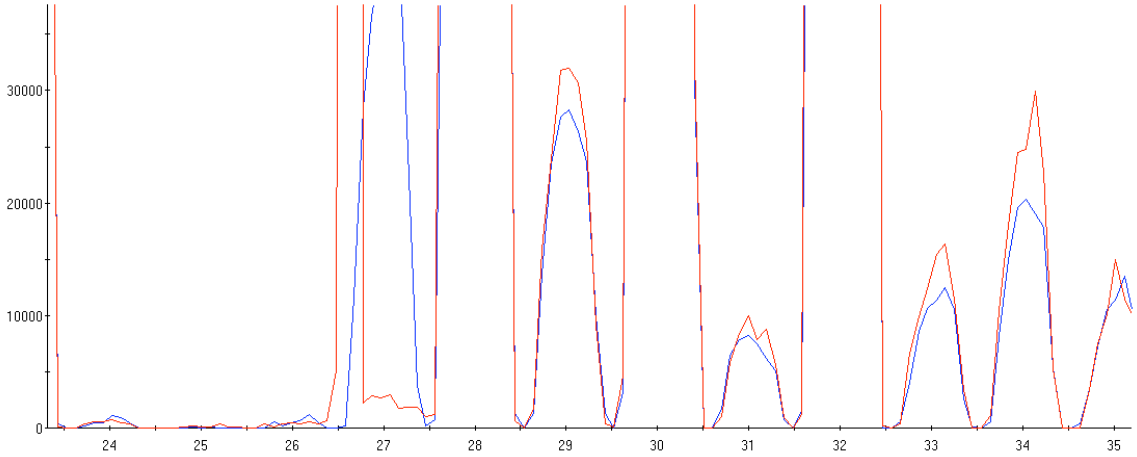

Figure 1. Mass scan over 24 to 35 amu, with and without laser ablation, on ultra-pure sapphire.

Another area of interest is the Sn signal area. Sn has many isotopes in scanned mass numbers from 113 to 124, with ^{118}Sn and ^{120}Sn being the most abundant and the ones most commonly used for Sn concentration determination. Clearly, the ablated sapphire trace showed small amounts of ions with mass numbers 118 and 120.

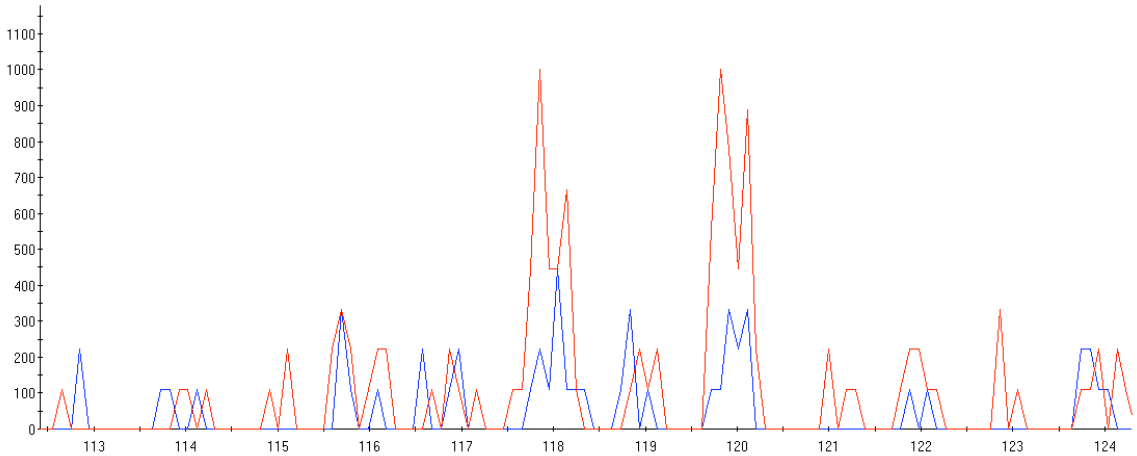

Figure 2. Mass scan over 113 to 124 amu, with and without laser ablation, on ultra-pure sapphire.

Three more line scan runs were performed to collect the commonly seen time slices representation of ICP-QMS data; the results are shown in figures 3 and 4. Figure 3 shows the time slices of ^{28}Si and ^{29}Si signals. The red line indicates when the laser started firing. Clearly, both traces clearly showed signal associated with the aerosol entering the plasma. Figure 4 depicts the time slices of ^{43}Ca and ^{120}Sn signal channel. It is expected to see AlO^+ ions that in

the plasma with alumina aerosol. $^{27}Al^{16}O^{+}$ has m = 42.97645 amu and it shows up in ^{43}Ca signal and this is exactly what we see in the top panel of figure 4. The ^{120}Sn signal is less prominent but still present in the lower panel.

These signals do not warrant the presence of interference, because even an ultra-high-purity sample still contains some trace elements. Checking the isotopic ratio of the elements in question against the natural isotopic ratio is the definitive stop to identify interference. As mentioned before, silicon has three stable isotopes existing in nature: ^{28}Si, ^{29}Si and ^{30}Si, and their natural abundance ratio should be 92.2%:4.7%:3.1%. Due to the overwhelming background at mass number 28, only the $^{29}Si/^{30}Si$ was examined in this study. In natural Si, the $^{29}Si/^{30}Si$ ratio should be 1.516. However, the ratio found in these high-purity sapphire time-slice runs averaged 0.414 for all three samples. The range of this ratio was 0.17 to 0.59, all significantly lower than the natural abundance. If these signals detected were really from a natural source of ^{29}Si and ^{30}Si, their relative abundance cannot be too far off from the natural ratios. The large deviation from the natural ratio proves that the signals observed in the run were heavily influenced by interference. The current data cannot be used to deduce the interfering ion species, and the appropriate tool to do this requires high-resolution ICP-MS.

Let us examine the Sn isotopes next. Tin has 10 isotopes, with mass numbers 112, 114, 115, 116, 117, 118, 119, 120, 122, and 124. Commonly used isotopes for tin determination are 118 and 120. We examined three in this study: ^{117}Sn, ^{118}Sn and ^{120}Sn. Two isotopic ratios were examined: $^{117}Sn/^{118}Sn$ and $^{118}Sn/^{120}Sn$. In nature, ^{117}Sn, ^{118}Sn, and ^{120}Sn have abundance ratios of 7.7%: 24.2%: 32.6%, therefore, the natural ratios should be $^{117}Sn/^{118}Sn$ = 0.318 and $^{118}Sn/^{120}Sn$ = 0.742. The ratios found in the experiment averaged 0.031 and 1.400, respectively, for all three samples. The range of $^{117}Sn/^{118}Sn$ was from 0.000 to 0.092, and that of $^{118}Sn/^{120}Sn$ was 0.367 to 2.769. In comparison, our typical run on NIST612 yielded $^{117}Sn/^{118}Sn$ = 0.316 and $^{118}Sn/^{120}Sn$ = 0.736. NIST610 run yielded $^{117}Sn/^{118}Sn$ = 0.312 and $^{118}Sn/^{120}Sn$ = 0.723. Again, this is a strong indication that the tin signals from the high-purity sapphire were in fact interference. The ratios from NIST glasses, however, indicate signals from a natural Sn source. Again, the nature of this interference is unknown and even more puzzling; the mass numbers of these interfering ions are much larger than any of the major elements in corundum Al and O, the Ar plasma gas and the environmental C, N and O. A cluster of $(Al_2O_4)^{+}$ will give a mass of 118, but the probability of forming a cluster decreases as the cluster size increases. Again, this will be a question for the high-resolution magnetic-sector mass spectrometer.

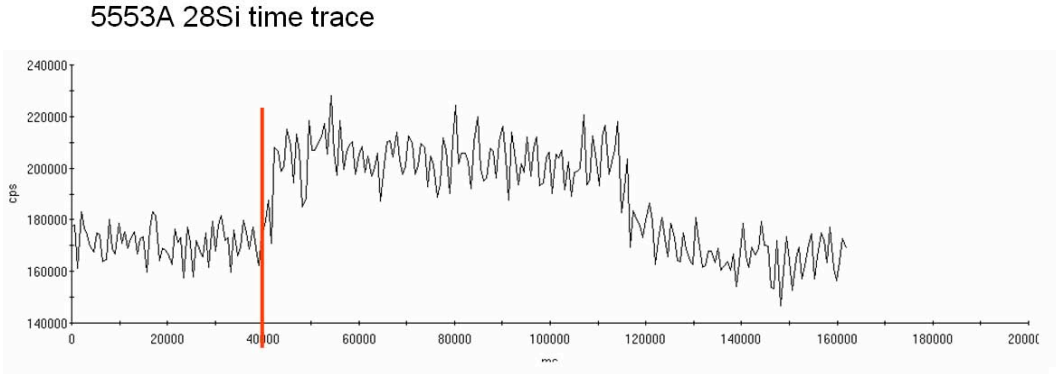

Figure 3. Time traces at mass 28 and 29 in an ultra-pure sapphire run.

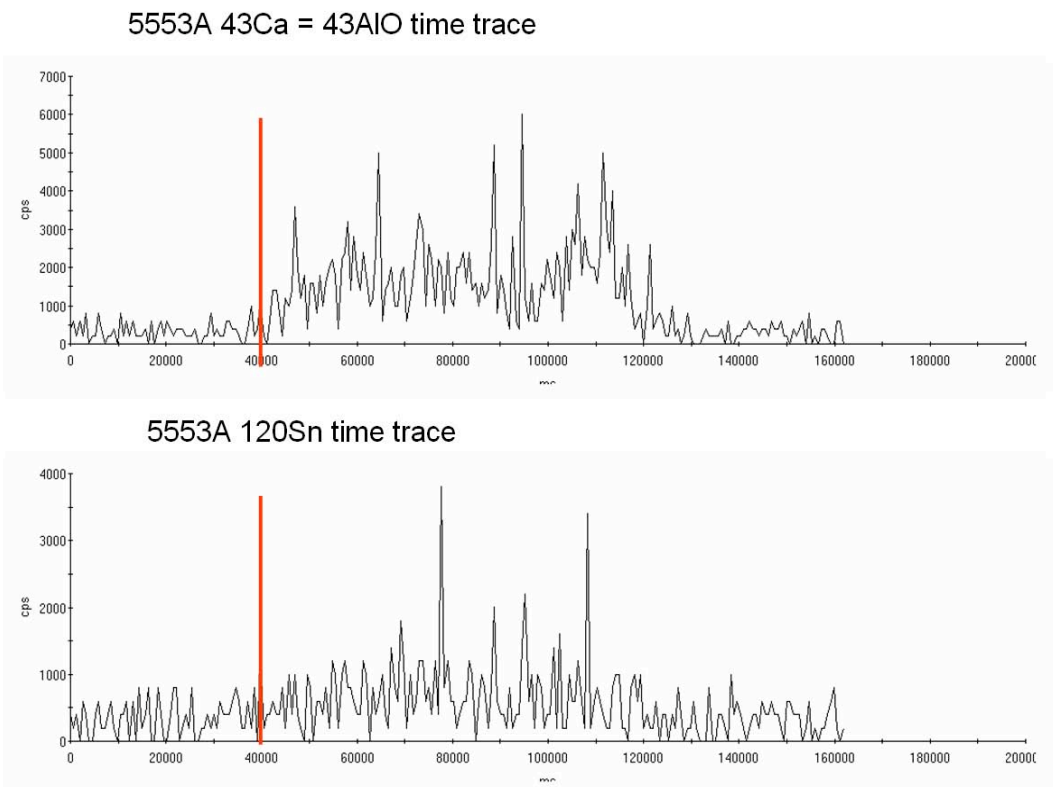

Figure 4. Time traces at mass 43 and 120 in an ultra-pure sapphire run.

A. H. Shen. Silicon detectability in corundum using LA-ICP-QMS (laser ablation–inductively coupled plasma–quadrupole mass spectrometry). News from Research, September 29, 2009. http://www.gia.edu/research-resources/news-from-research

The next question is how much silicon is detectable by LA-ICP-QMS. Before answering this, two concepts should be explained. The first is Limit of Detection (LOD), which the International Union of Pure and Applied Chemistry (IUPAC) defined as “A number expressed in units of concentration (or amount) that describes the lowest concentration level (or amount) of the element that an analyst can determine to be statistically different from an analytical blank” (1978). The second figure is Limit of Quantification (LOQ), the lowest concentration that can be reliably quantified. IUPAC and the American Chemical Society further defined the LOD as three times the standard deviation of the blank divided by the sensitivity. The actual equation we used in our analysis was from Longerich et al.(1996). LOQ is used extensively in the environmental, medical and food science communities (see for example, Corley, 2003 and the references therein). The LOD only indicates whether an element (or substance) is present. Statistically speaking, however, LOD is too low a boundary to avoid a “false negative” (or type II, beta) error. Statistics shows a value of LOD still has a 50% chance of a “false negative” error (i.e., indicated as below the detection limit, but in fact present). Common practice defines the LOQ to be 10 times the standard deviation of background level divided by the sensitivity, which is ~ 3.3 times of LOD. This value will reduce the “false negative” error probability to well below 1%. Therefore, we report LOD (or detection limit, DL) but use LOQ as the real boundary of reporting values for unknown samples.

In the next experiment, we included the ultra-pure sapphire in a typical corundum run, which includes a gas blank as well as the GIA corundum standards. To see the effect of including ultra-pure sapphire as the true blank, the same data set was processed twice: first with a gas blank and the second time with an ultra-pure sapphire blank in the calibration. The results are summarized in table 1. All Si and Sn concentrations were calibrated against NIST610 glass. The blue columns are the concentrations calculated using the ultra-high-purity sapphire blank, and the yellow columns were calculated using a gas blank. The LOD and LOQ values for each isotope are listed in the bottom rows in brown and red numbers. It is obvious that the reported Si and Sn concentrations in the yellow columns were dramatically lower in the blue columns. Why? The main reason is that by including the ultra-pure sapphire blank, the additional interference signals shown in figures 1–4 are now shifting the calibration lines away from the origin (because most gas blank calibration points are either on or very close to the origin). Thus these new calibration lines dramatically reduced the Si concentrations over the wide color range of corundum, providing more reliable values. Most of the samples’ Si and Sn concentrations have been reduced below the quantification limit. Our instrument can detect as low as 20 ppmw for Si and 0.070 ppmw of Sn, but 66 ppmw for Si and 0.23 ppmw for Sn are the lowest concentrations we can report confidently. To determine Si concentrations lower than 66 ppmw in corundum using our instrument, one would need to use a high-resolution ICP-MS, SIMS or some other analytical instrument.

Notice some of the samples do show some silicon concentrations, and that they vary from 100 ppmw to over 500 ppmw in the same sample. All the samples were natural sapphires and may contain inclusions or heat treatment residue. It is quite possible that some of the laser spots hit the inclusions or residue.

A final source of error in this analysis needs to be identified here. The detection limits quoted here are based on calibrations against NIST610 glass using Al as internal standard. They are

used because of the lack of reliable Si standard in corundum. Therefore, such values represent the best we could obtain experimentally, but may vary significantly from the actual value. These values could be further refined if a corundum-based Si or Sn standard were used.

Finally, one might reasonably question the stability of the interference level at 28 and 29 amu from day to day. To answer this question, we documented eight experiments spanning more than five weeks. The data points in figure 5 were calculated concentrations of interferences at 28 and 29 amu from the high-purity sapphire as unknown, using NIST 610 and 612 glasses and the gas blank as calibration. The error bars were ± 1σ (standard deviation from the time trace). One can clearly see there is no dramatic difference from day to day. In fact, one can fit a horizontal line through all points within their error bars. Therefore, we conclude the interferences on these two isotopes are stable over time.

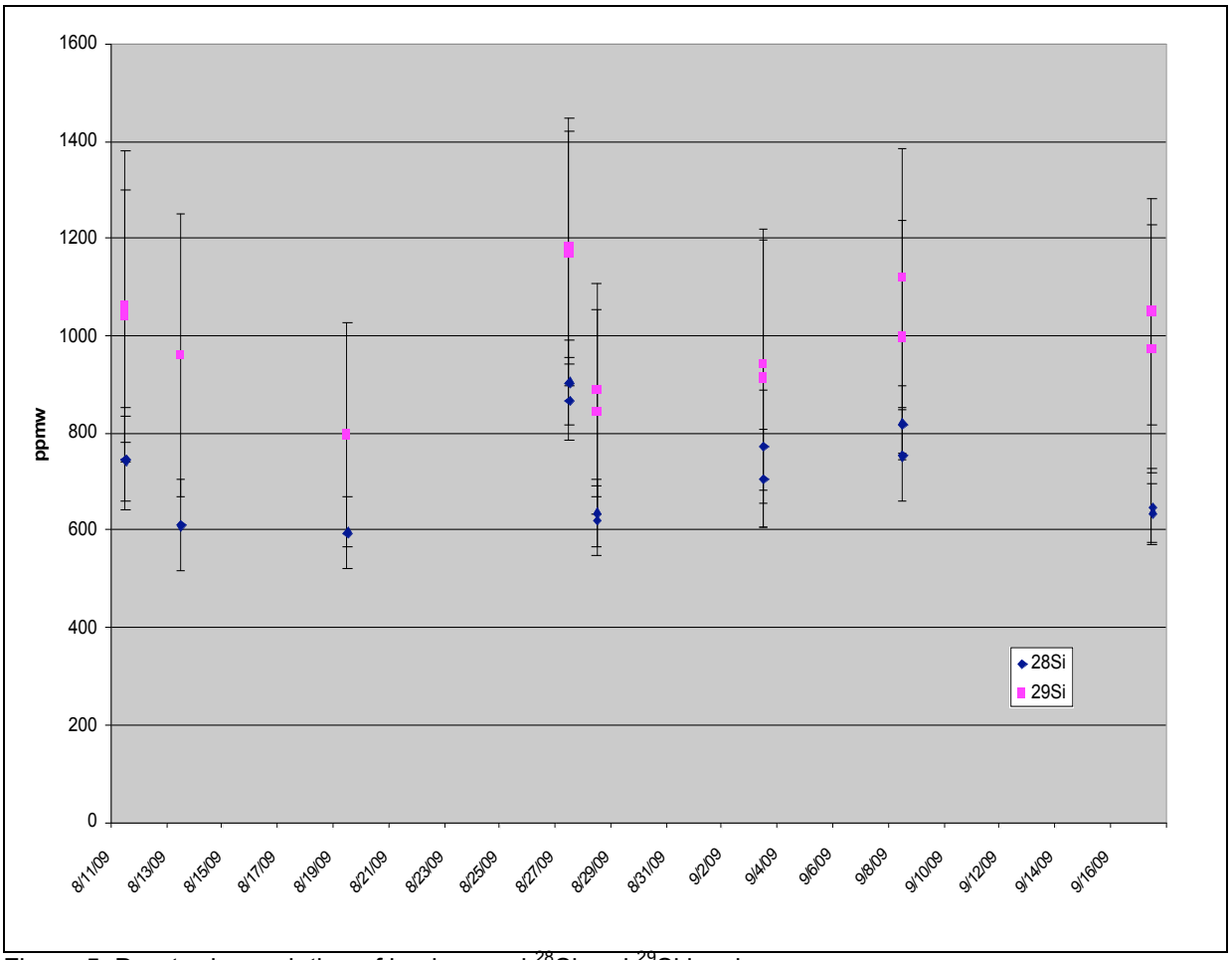

Figure 5. Day-to-day variation of background ^{28}Si and ^{29}Si levels.

In conclusion, it is clear that some ion species generated in the ICP with ablated corundum aerosol create additional interference to Si. Therefore, any laboratory using LA-ICP-QMS to analyze Si must (1) include a high-purity sapphire in their corundum run as blank sample, and

(2) perform careful analysis of detection and quantification limits to know exactly the LOD and LOQ of the pertinent elements.

References

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Table 1

Sample	28Si Ppmw	28Si ppmw	29Si ppmw	29Si ppmw	118Sn ppmw	118Sn ppmw
dark blue sapphire sp1	1180	436	1640	643	1.42	0.82
dark blue sapphire sp2	1300	566	1490	490	1.02	0.41
dark blue sapphire sp3	843	103	1250	bql	1.39	0.79
ruby1 sp1	615	bql	937	bql	0.70	bql
ruby1 sp2	644	bql	992	bql	0.42	bql
ruby1 sp3	657	bql	960	bql	0.62	bql
orange sapphire sp1	732	bql	1080	bql	1.11	0.51
orange sapphire sp2	689	bql	998	bql	0.87	0.27
orange sapphire sp3	707	bql	1000	bql	0.84	0.24
pink sapphire sp1	237	bql	bql	bql	0.59	bql
pink sapphire sp2	620	bql	814	bql	1.41	0.80
pink sapphire sp3	689	bql	949	bql	0.97	0.37
ruby2 sp1	656	bql	966	bql	0.49	bql
ruby2 sp2	711	bql	959	bql	0.39	bql
ruby2 sp3	820	79.8	1100	bql	0.60	bql
ruby3 sp1	bql	bql	bql	bql	0.50	bql
ruby3 sp2	345	bql	480	bql	0.50	bql
ruby3 sp3	538	bql	828	bql	0.57	bql
ruby4 sp1	334	bql	bql	bql	0.49	bql
ruby4 sp2	569	bql	726	bql	0.48	bql
ruby4 sp3	675	bql	980	bql	0.58	bql
LOD	**20**	**20**	**85**	**85**	**0.070**	**0.070**
LOQ	**66**	**67**	**279**	**280**	**0.23**	**0.23**