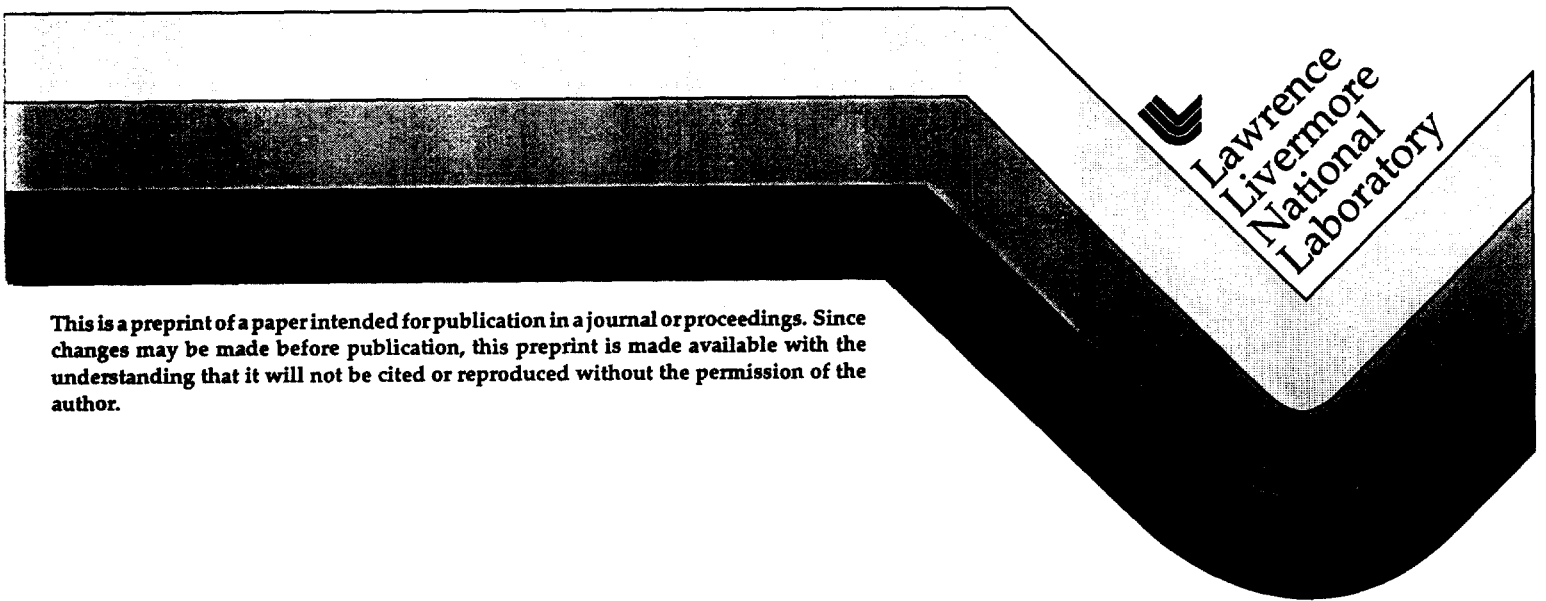232450

Depth Profiling of Polishing-Induced Contamination on Fused Silica Surfaces

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Depth profiling of polishing-induced contamination on fused silica surfaces*

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ABSTRACT

Laser-induced damage on optical surfaces is often associated with absorbing contaminants introduced by the polishing process. This is particularly the case for UV optics. In the present study, secondary ion mass spectroscopy (SIMS) was used to measure depth profiles of finishing-process contamination on fused silica surfaces. Contaminants detected include the major polishing compound components (Ce or Zr from CeO_2 or ZrO_2), Al present largely because of the use of Al_2O_3 in the final cleaning process, and other metals (Fe, Cu, Cr) incorporated during the polishing step or earlier grinding steps. Depth profile data typically showed an exponential decay of contaminant concentration to a depth of 100-200 nm. This depth is consistent with a polishing redeposition layers formed during the chemo-mechanical polishing of fused silica. Peak contaminant levels are typically in the 10-100 ppm range, except for Al which often exceeds 1000 ppm.

A strong correlation has been shown between the presence of a "gray haze" damage morphology and the use of CeO_2 polishing compound. It has not been proven, however, that linear absorption by CeO_2, or any other contaminant, is the relevant damage mechanism. Simple thermomechanical calculations show that for the contaminant levels present, temperatures high enough to cause damage are only likely if the contaminant was present as particles with diameters of 10-30 nm. We are not able to prove or disprove the presence of such particles. No strong correlation between high levels of Ce, or any other contaminant, and low damage threshold is observed. In fact one of the strongest indications of a correlation is between increased damage thresholds and _increased_ Zr contamination. This suggests that the connection between redeposition layer contamination and laser damage threshold is not simply an absorbing contaminant issue.

Key words: CeO_2, contaminants, fused silica, polishing, surface, 355 nm.

1. INTRODUCTION

The laser damage threshold of transmissive UV optical components is typically limited by the polished optical surfaces. One of the primary mechanisms proposed for the damage of polished surfaces is thermo-mechanical damage due to absorption by polishing contaminants in the near-surface (100 nm) region of the optic. It is well known that polishing of fused silica is a chemo-mechanical process which results in the formation of a thin redeposition or Beilby layer.[1] Damage at polished surfaces has been associated with contamination by the polishing compound itself. Estler, et al.[2] have shown, using resonance ion mass spectroscopy, that CeO_2 is present in a surface polished with that material. They presented further data showing that leaching the surface with acid can both reduce the ceria level and increase the laser damage threshold. We have observed at LLNL that surfaces polished with CeO_2 shown a "gray haze" damage morphology when illuminated at fluences above approximately 8 J/cm² for 3 ns, 355 nm laser light. The gray haze damage morphology consists of a high density of shallow pits in the surface, as shown in figure 1.[3] The peak UV fluences required for optics on the National Ignition Facility (NIF) is 14 J/cm². We have recently found that the gray haze damage can be reduced or eliminated by eliminating the ceria-polishing-induced redeposition layer through either of two methods: a) substitution of ZrO_2 (a non-absorbing material at 355 nm) as the polishing compound, or b) removal of the surface layer with a chemical or ion etch.[4] The shallow nature of the gray haze damage and it's connection with the redeposition layer support a simple absorbing contaminant model for gray haze damage initiation.

The purpose of the present work was to provide a more thorough analysis of redeposition layer contamination and its correlation to laser damage. Secondary ion mass spectroscopy was used to study concentration depth profile for several potential contaminants. The potential contaminants were identified in part by emission spectroscopy of polishing slurries. Contamination data from finished surfaces provided by several commercial vendors as well as LLNL (sources A-E) was correlated with laser damage threshold data from the same parts.

It should be noted that while the redeposition layer appears to play a significant role in UV laser damage to transmissive optics, other damage initiators can also play a role. These initiators include subsurface damage,[5] surface scratches,[6] surface contaminants,[7] and bulk defects.

2. REDEPOSITION LAYER CONTAMINATION STUDIES

Redeposition layer contaminant levels were studied as a function of depth using Secondary Ion Mass Spectroscopy (SIMS). Table 1 gives the experimental parameters for the SIMS depth profiling experiments. Before depth profiling is begun the sample is coated with 10-15 nm of carbon to prevent surface charging.

Table 1: SIMS depth profiling parameters

Ion gun	1-10 nA $^{16}O^-$
Scan area	100 µm x 100 µm
Sampling area (lateral resolution)	30 µm diameter centered in scan area to reduce edge effects
Depth profiling rate	20-25 sec/nm
Profile depth	200 - 400 nm
Vertical resolution	~10 nm based on integration time
Detection limit	~0.1 ppmw

Figures 2a and 2b show typical SIMS profiles for Ce contamination of a polished surface. The peak Ce concentration is located at the surface or at depths down to ~30 nm. The Ce concentration falls off to ~10% of the peak typically after 80-100 nm. Ce concentrations ranging from 2-390 ppm have been detected. For most samples the Ce concentration is <30 ppm.

Depth profiles indicate that Ce was not the only, or even the major contaminant, in the redeposition layer. Figure 3a and 3b show semi-long plots of contamination level vs. depth for Al, Ce, Cr, Cu and Fe for two sites on a sample from source E. Note that Ce shows the lowest contaminant levels. The Al profile shows the steepest slope, consistent with surface contamination caused by final cleaning operations. In some cases Fe and Cr show parallel slopes. This may suggest contamination by stainless steel present in the polishing equipment. The smooth depth profile measured in the samples indicate that if the contamination was due to particles in the redeposition layer, these particles would be smaller than 30µm in diameter.

Comparison of figures 3a and 3b show that the concentration levels of a given element vary from site to site. Figure 4 shows the range of peak contaminant levels that were observed in tests on several sites on samples from two sources. The sampling area for each site is 30 µm in diameter while the diameter of the laser beam used in damage testing is on the order of 1 mm in diameter. This non-uniformity of the contaminants may make correlation of local contaminant levels and damage thresholds difficult. Also note that the gray haze damage shown in Figure 1 shows damage initiation sites of ~1 µm in diameter occurring at separations of ≤10 µm. A probe with resolution of 30 µm could not resolve individual contaminant sites, again complicating the correlation of SIMS data with damage threshold data.

Our main interest was the level of contamination after the final polishing process. However, in order to determine the sources of the redeposition layer contamination we also examined samples from vendor D after completion only up to a loose abrasive grind step and a rough polishing step. Figure 5 shows that many contaminants are present in the fused silica surface prior to the final polishing step. The depth of the contaminated layer after grinding is only ~200 nm. This surface layer would be completely removed during a typical polishing operation that would remove several μm of material. We have not determined if the contamination present in a final polished sample is due to the polishing step itself or is a result of redeposition of contaminants introduced to the sample during previous finishing steps. There is some evidence, however, that the near-surface contaminant levels are determined largely by the most resent finishing process. For example, in Fig. 5 the concentration of Cu is high after the grinding step which uses a copper lap, but is decreased by two orders of magnitude after the polishing step.

3. COOLANT AND SLURRY CONTAMINANTS

ICP-emission spectroscopy was used to measure contaminant levels in blanchard coolant and grind/polish slurry solutions. Two types of impurity measurements were made: a) "filtrate": a solution that was filtered to remove particles and b) "leach": a solution formed by leaching the original slurry so as to include contributions of particles. The leached samples were prepared using the following procedure:
1) evaporate to dryness, 2) heat with aqua regia until dry (leach particles), 3) reconstitute with 0.2 M HNO_3, 4) filter through 0.45 μm syringe. Figure 6 shows elemental concentrations for leached blanchard, grind and polish solutions. Note that Ce levels are high for polishing steps as expected. Ca, Mg and Na are high in blanchard solutions due to surfactants used in the coolant. In general, many of the results are comparable for the two sample preparation techniques. However, the heavy metals (such as Fe and Cu) as well as the major constituents (Al in the Al_2O_3 grind solution or CeO_2 in the polish slurry) show higher concentrations in the "leach" then they do in the "filtrate". This suggests that some of the impurities are particulate rather than being dissolved in the slurry. We have not yet made a correlation between relative contaminant levels in the slurries and the corresponding surfaces.

4. ABSORPTION AND HEATING BY TRACE ELEMENTS IN GLASS

In order to determine the feasibility of redeposition layer contaminants initiating laser damage in fused silica surfaces, the optical absorption properties of the contaminants must be known. The most complete set of absorption spectra for elements in glass that we found was provided by Smith and Cohen.[8] That paper measured spectra for $Na_2O \cdot SiO_2$ glass doped with various elements under different oxidation conditions. We reduced that data to provide, in Fig. 7, a plot of absorption cross-section for the elements identified in the redeposition layer and slurry contamination studies. The value shown is the highest absorption level in cases where data was given for both reducing and oxidizing conditions. In all cases except for Ce the absorption coefficient was higher for the oxidizing conditions. The plot shows that the elements of most concern are Ni, Fe, Ce and Cr. Absorption cross sections of other elements including Al, present due to cleaning processes, and Zr, from substitution of ZrO_2 for CeO_2 as a polishing compound, are lower by over two orders of magnitude. For comparison, CeO_2 absorption cross-section of $3.0x10^{-18}$ cm^2/ion and of $5.0x10^{-19}$ cm^2/ion have been reported elsewhere [9 and 10, respectively]. This level of variability in absorption cross-section does not influence the conclusions of this paper.

It is not clear if the contaminants in the redeposition layer are present as a uniform dopant or as discrete particles. Particles are suggested by the discrete nature of the gray haze pit morphology. The ICP-emission spectroscopy analysis of the slurries (leach vs. filtrate) show that the slurries contain particles of material other than just the main polishing component. The smooth depth profiles observed for the contaminants suggest, however, that any particle included in the redeposition layer is less than 30 μm in diameter.

In order to determine the likely distribution of damage-initiating contaminants, simple particle heating calculations for various distributions of contaminant elements, in oxide form, were calculated.[11] These calculations include conduction effects, but not radiation effects. Table 2 shows the estimated temperature rise for various levels of CeO_2 doping and various sizes of CeO_2 particles in SiO_2 when illuminated with a

10 J/cm^2, 3 ns pulse at 355 nm. The calculations show that particles on the order of 10 nm in size would easily heat the glass to a failure point. Uniformly distributed CeO$_2$ at levels measured by SIMS would be rather benign.

CeO$_2$ particle diameter	Temperature rise, °C (r=0)
1 nm	45
3 nm	440
10 nm	4,200
32 nm	37,000
100 nm	230,000

CeO$_2$ dopant level	
100 ppm	9
1000 ppm	92

Table 2: Estimated temperature rises for several particle sizes and dopant levels of CeO$_2$ in fused silica illuminated with 15 J/cm^2, 3 ns, 355 nm pulses. For particles, the temperature rise is for the center of the particle. CeO$_2$ absorption coefficient: 72,000 cm^{-1}.

5. CORRELATION TO LASER DAMAGE THRESHOLD

We attempted to find a correlation between the gray haze damage threshold and the level of the various contaminants in the redeposition layer for a wide range of samples from the five different vendors. No obvious correlation was observed. In fact one of the highest damage threshold parts we have measured showed very high levels of non-primary-component contamination, particularly iron. Figure 8a and 8b show plots of damage threshold vs. contaminant level for six surfaces polished by vendor B. Three surfaces did not show any gray haze. The correlation of contaminant level to damage threshold appears stronger for Zr than for Ce. The increase in damage threshold with increasing Zr level cannot be explained using any type of absorption argument.

6. CONCLUSION

Chemomechanically polished surfaces have an approximately 100 nm thick redeposition layer which is contaminated by a number of elements present in the polishing slurry. The major contaminants are often Cu, Cr, and Fe rather than the primary polishing component, Ce or Zr. Contaminant concentrations may be as high as several hundred ppmw. High levels of Al are attributed to the final cleaning process.

Estimates of temperature rises based on highest measured contamination levels and published absorption data are <100°C, assuming uniform doping of the redeposition layer. This small temperature rise is not likely to initiate laser damage. Temperature rises of greater than 2000°C are expected, however, if the contaminant is present as particles of >10 μm diameter. Particles larger than 30μm are not believed to be present based on smooth SIMS profiles. No direct evidence of particles in this size range is available.

The elimination of gray haze damage through the substitution of ZrO$_2$ for CeO$_2$ as the polishing compound suggests that CeO$_2$ plays an important role. Since other contaminants of similar absorption properties are present at equal or higher concentrations, it is not clear that CeO$_2$ absorption is the cause of gray haze damage.

Correlations of damage threshold to contaminant level are weak at best. In fact the strongest correlation appears to be an increase in damage threshold with increasing Zr levels. This correlation cannot

be explained based on absorption arguments. It instead suggests that the polishing compound influences damage threshold through some other effect such as sub-surface morphology.

5. ACKNOWLEDGMENTS

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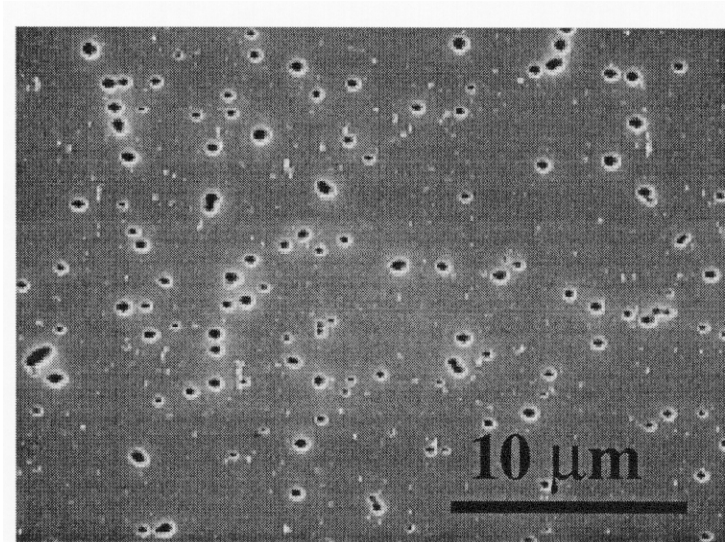
Figure 1: SEM micrograph of gray haze damage created by 351 nm, 7 ns illumination of a polished fused silica surface. [3]
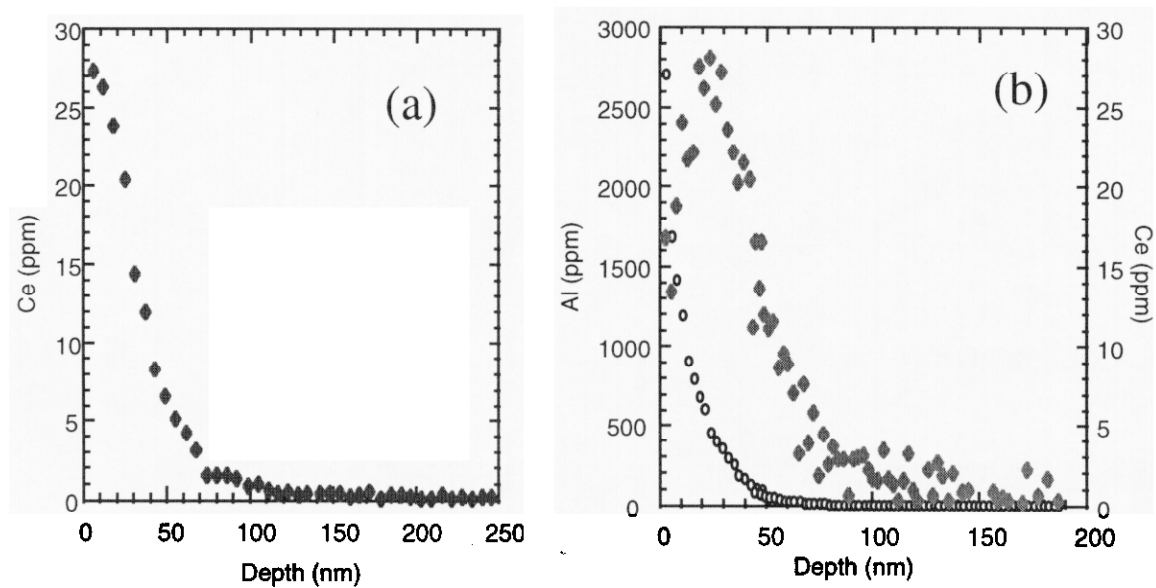

Figure 2: SIMS depth profiles of Ce and Al concentrations inside the deposition layer of polished fused silica surfaces from (a) source A and (b) source B.
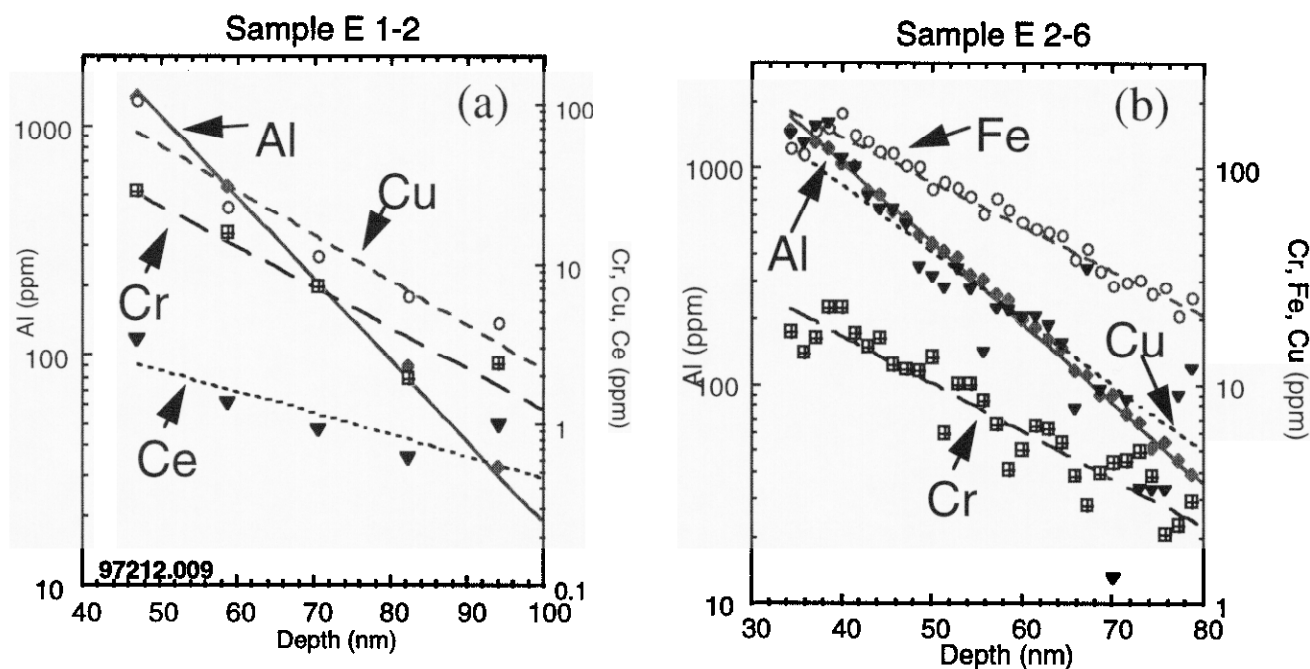
Figure 3: Semi-log plots of contamination depth profile of several elements at two sites on a polished fused silica substrate from source E. (a) sample E 1-2 and (b) sample E 2-6.
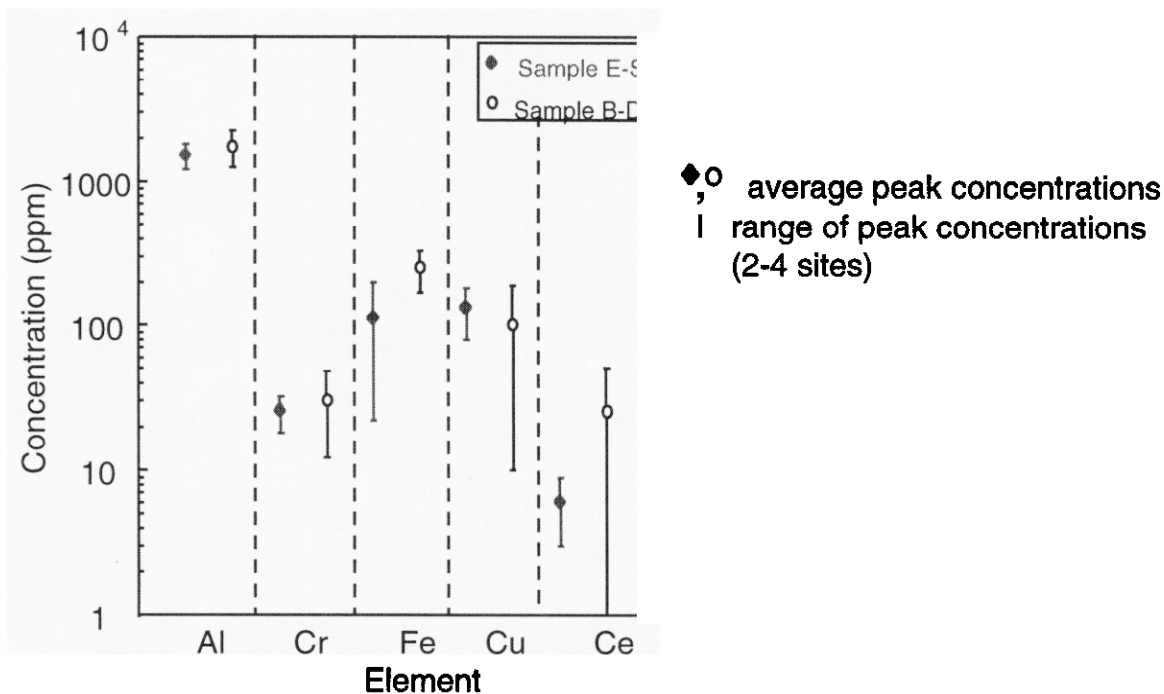

Figure 4: Range of contaminant levels measured on polished fused silica surfaces from two different vendors. Averages is calculated for 2 to 4 SIMS measurements on different 30 μm diameter areas.

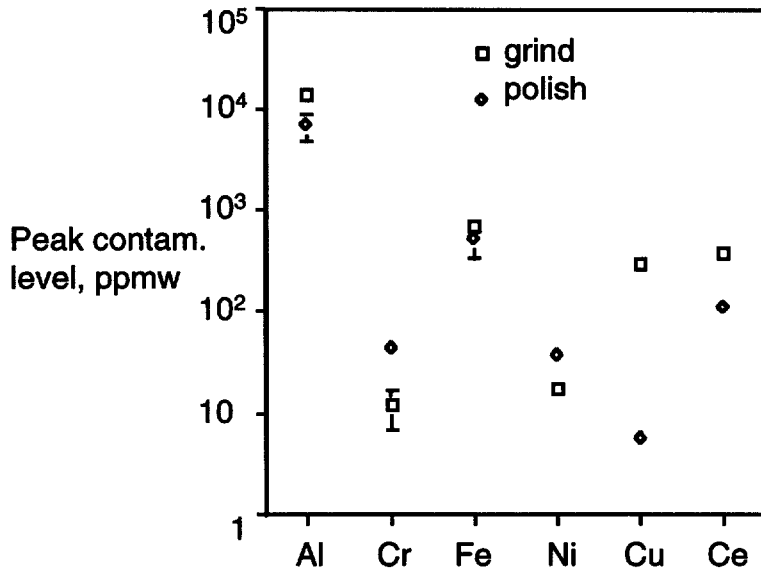Figure 5: SIMS peak contamination levels measured after loose abrasive grind and CeO₂ polishing steps on fused silica substrates from source B..
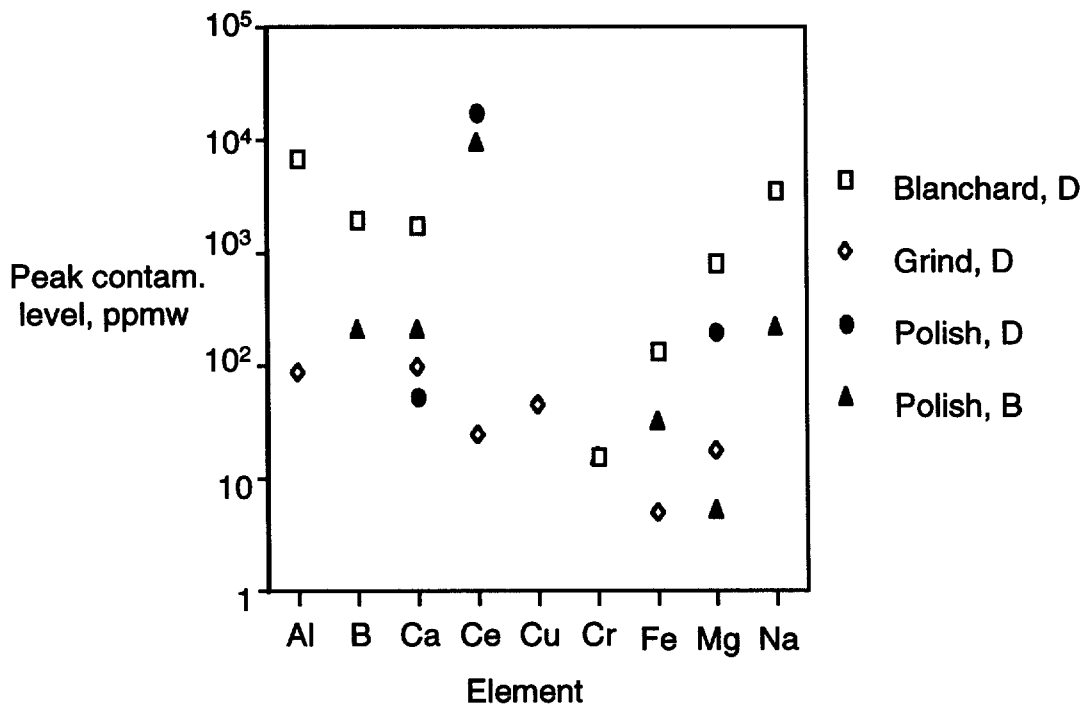

Figure 6: Contamination levels, measured using ICP- emission spectroscopy, for various slurry and coolant solutions. Solutions were leached to include contributions from particulates in the solution. Samples from sources B and D.
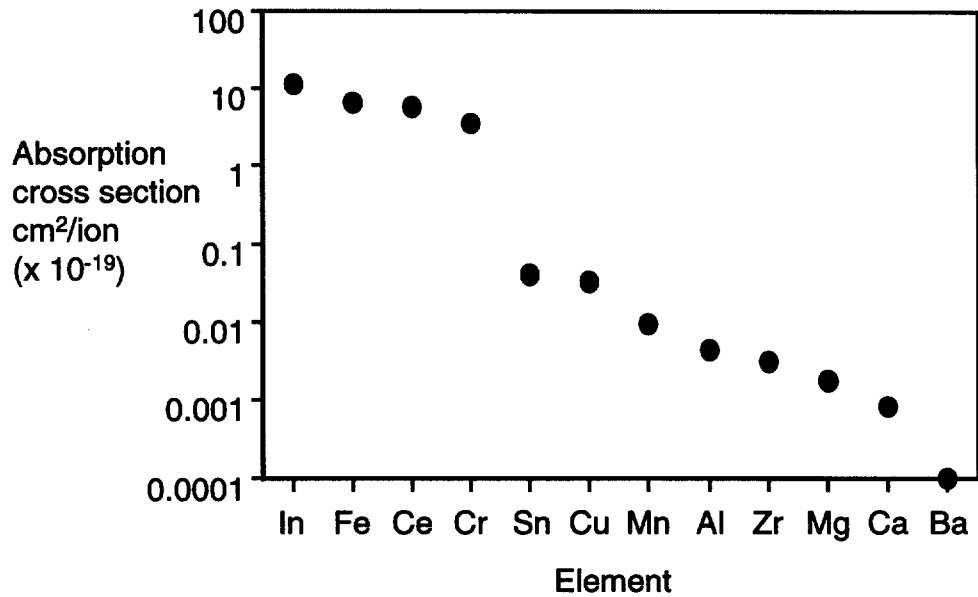
Figure 7: Absorption cross-sections for contaminants identified in redeposition layer and slurry solution analysis. Values were calculated from absorption spectra reported by Smith and Cohen[8] for trace elements in $Na_2O \cdot SiO_2$ glass. Glass formed under oxidation conditions provided the highest cross-sections (shown here) except for the case of Ce where reducing conditions provided higher thresholds.
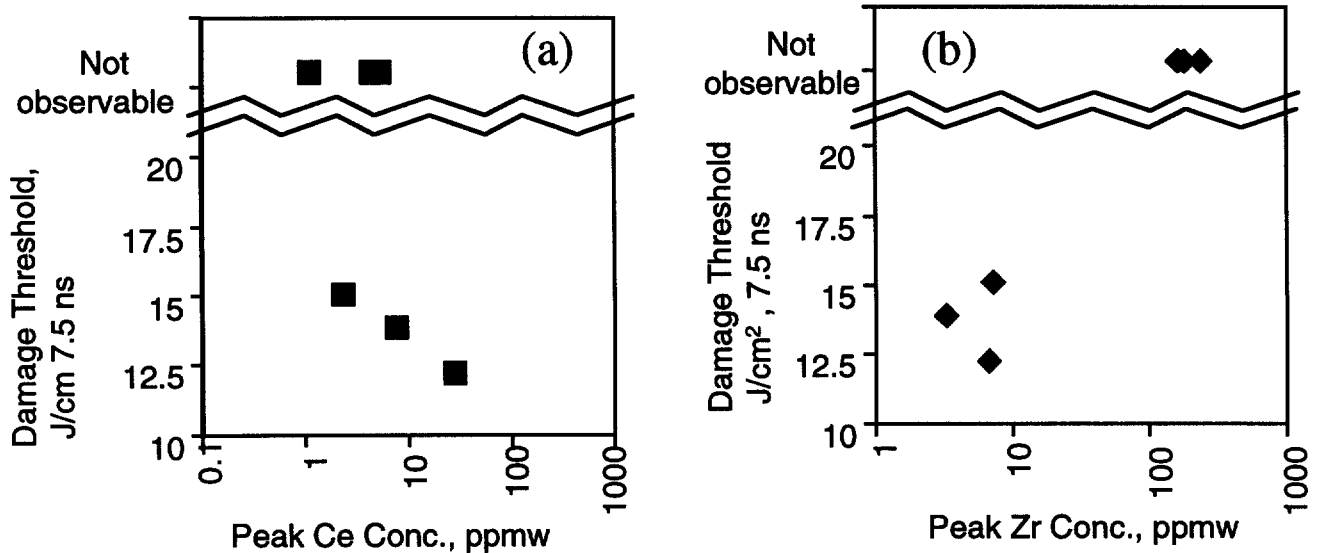

Figure 8: Gray haze damage thresholds vs.. peak concentration of (a) Ce and (b) Zr (measured using SIMS) for several samples from source B. Data from samples B1, 5, 6, 8.