Understanding the Stability of Barium-Containing Ceramic Glazes

This cover page is meant to focus your reading of the sample proposal, summarizing important aspects of proposal writing that the author did well, or could have improved. Review the following sections before reading the sample. The proposal is also annotated throughout to highlight key elements of the proposal’s structure and content.

<table>
<thead>
<tr>
<th>Proposal Strengths</th>
<th>Areas for Improvement</th>
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<tbody>
<tr>
<td>Student does an excellent job defining key technical jargon in simple terms.</td>
<td>Methods section begins generally and then becomes specific. Instead, you can save space by getting right into what you are doing specifically.</td>
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<tr>
<td>Student gives background both from what the lab has done so far and beyond the lab in the field at large.</td>
<td>Student justifies methodologies in methods section. This information could be moved to the background section, so that methods are focused on the actions of the student researcher only</td>
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<tr>
<td>Student’s part of the project is clear by end of the introduction (called background by student)</td>
<td>There is not a clear view of how the student’s 8 weeks will look. Giving a rough timeline, or at least putting tasks in order would help, but you do not need to offer a week-by-week schedule.</td>
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<tr>
<td>Each component of the student’s methodology is justified in terms of what aspect of the research question it helps to answer.</td>
<td>Student should give a clear picture of what the analysis looks like for their project.</td>
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</tbody>
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Other Key Features to Take Note Of

Section titles and headers are not necessary in any URGs. Your title will appear on an automatically generated cover page, and the review committee is familiar with the grant forma. Therefore, section titles are unnecessary.

Often a student in a lab will be proposing their own small part of a lab’s larger project. As such, sometimes what the lab has done so far will be part of the background. It is important though that the student does not attempt to propose/justify the larger project, but instead narrows the focus on only what part the student themselves have.
Background. Ceramic glazes are used both as decoration and as a coating to seal porous clay in order to contain foods and liquids. Glazes are a mixture of aluminosilicate matrices and various metal oxides. The aluminosilicate gives the glaze its strength, while the metal oxides alter the melting temperature, color, or texture of the glaze. Glazes are applied to the surface of formed clay and then fired in a kiln. If glazed pottery is intended for use with food, the product must pass FDA guidelines for lead and cadmium content. Lead exposure can lead to developmental delays in children. Cadmium exposure over time can lead to renal damage.

The Northrup research group began research on pottery glazes after analyzing pottery samples from Mexico. The group was surprised to find high barium levels in glazes where lead was intentionally avoided, suggesting that barium may be replacing lead in some traditional pottery. While barium is a toxic metal that can lead to respiratory muscle paralysis, nausea, and diarrhea, the FDA does not regulate its use in pottery. Many researchers have investigated the safety of lead glazes, but the safety of barium glazes is a novel research field. Subsequent research done by the Northrup group has focused on pottery glazes containing barium. We have determined that some barium glazes are safe but others are not. Building upon this research, my focus this summer will be to determine why barium glazes are or are not safe.

Previous Research. Multiple factors can affect the stability of barium in the ceramic-glaze matrix, such as firing temperature, firing environment, and glaze composition. To begin, increasing the temperature at which pottery is fired will generally increase the stability of the ceramic-glaze matrix. Unfortunately, kilns that fire at high temperatures, as measured in “Cones” by potters, are often more expensive. The only published research on barium glazes has shown that glazes fired at Cone 11 leached at least five times less barium than the same glazes fired at Cone 10. Most of the Northrup group research has been conducted with pottery fired at Cone 6 (1222 ºC), which is a common firing temperature for potters because it is attainable with affordable kilns. However, Cone 6 fires at too low a temperature to ensure that barium is always safely stable in the matrix. We have shown that some glazes fired at Cones 5, 6, or 7 are stable and others are not.

Firing environment also can affect the stability of barium glazes. Pottery can be fired either under oxidizing (oxygen rich) or reducing (oxygen poor) conditions. We found that firing in reducing conditions stabilized barium in some glazes but not in others. My research on the molecular form of barium in these fired glazes will help to explain these results.

Glaze composition, the raw materials that are mixed to create a glaze, can affect the stability of barium in the fired product. DeBoos found that the stability of barium-containing glazes depended on the silica and alumina content. We have found that the amount of barium leached from the fired glaze depends at least as much on the presence of other metals as on the quantity of barium in the glaze. A high presence of zinc causes barium to be leached from a glaze in high quantities. The presence of copper has a similar effect but with less consistency than zinc. An understanding of these effects will require an investigation of how the presence of other elements affects the molecular form in which barium exists in a fired glaze. Barium is introduced to the glazes in the form of barium carbonate. After firing at high temperatures, barium is thought to be either in the free form of barium oxide or incorporated into the aluminosilicate matrix. We have done extensive amounts of glaze production, leading to a current collection of glazed tiles that spans many different firing environments, firing temperatures, and glaze recipes. These glazes have already been analyzed for leached barium content to determine their safety. The molecular composition is likely to be dependent on these various glaze formation parameters. This provides me with a wide range of sample variations with which to study why certain glazes are safe despite their barium content.
Research Plan. I will collect and analyze data from various types of microscopy to study the molecular composition of barium glazes, and thus understand their safety. I have begun using various techniques to map the composition of leached and unleached barium glazes at their surfaces in order to begin to understand the fired glaze, elementally and molecularly. Scanning electron microscopy (SEM) has been used to analyze cross-sections of a barium and zinc glaze fired under reducing conditions and under oxidizing conditions. SEM back-scattered signal has shown zinc and barium to be present in similar locations in both the oxidized and reduced glazes. This is surprising based on their different leaching results and based on the SEM finding that the tile fired in an oxidizing environment is much more crystalline. The elemental composition is not sufficient to understand the behavior of the glazes after firing, and other types of analysis will be required this summer to understand the molecular composition.

This summer, I will use infrared and Raman spectroscopy, two vibrational spectroscopy techniques that can be used to study the molecular composition of the glazes. They detect vibrational absorption frequencies characteristic of specific molecules. These two spectroscopy techniques are complementary, probing molecular composition in different ways. While infrared spectroscopy provides advantages in avoiding molecular fluorescence that could obscure important vibrational frequencies, Raman spectroscopy is typically more useful for inorganic compounds. Its ability to probe lower vibrational frequencies is useful for the metal oxides likely to be in glaze samples. I am learning to use a Fourier Transform Infrared (FTIR) microscope to study the vibrational structure of molecules in specific areas of glazed tile surfaces. Preliminary results for glazes with varying amounts of barium and zinc have shown different molecular vibrations in visibly leached areas of the glaze compared to visibly unleached areas. I will couple these infrared data with Raman spectroscopy to study the molecular composition of the visibly different areas.

With URG funding this summer, I will use SEM, FTIR microscopy, and Raman microscopy analysis techniques to provide complementary information about a variety of pottery glazes prepared with specific compositions and firing conditions. Work will begin on barium glazes in which the amount of zinc introduced has been found to affect the barium stability. An understanding of the molecular composition of these glazes will help to explain why this glaze can be made safer by reducing the zinc content. Microscopy studies will also begin on barium glazes containing copper and mixtures of copper and zinc where observed leaching behavior has been less consistent, indicating a more complex interaction between the various metals. The infrared and Raman spectra I acquire for these glazes will be compared to spectra acquired for a barium-containing frit, a high temperature fired mixture of barium, aluminum, and silica, known to stabilize barium in a pottery glaze. This will help our understanding of barium’s molecular composition in forms stable to acid leaching. As I will be using shared instruments, my scheduling will involve running SEM, FTIR and Raman spectroscopy experiments in parallel. This will ensure my eight summer weeks are used efficiently and productively. I also will spend a significant amount of time analyzing and comparing spectroscopic patterns from the three instruments in order to understand the elemental and molecular composition of the various fired glazes and thus why certain glazes are or are not safe.

Qualifications. At the start of the summer, I will have spent two academic years working in the Northrup group as a Chem-399 course. I am experienced in glazing pottery, ICP-AES analysis, and SEM analysis, and I am becoming experienced in FTIR microscopy. I will become experienced in Raman microscopy. I am also experienced in interpreting data from these various instruments. Courses I have taken as a student in the chemistry major program also have prepared me for this research, such as Chem-220 (Introductory Instrumental Analysis). I have learned the instrumentation and methodology necessary to do this research properly. Additionally, I intend to continue this research beyond this summer to write a senior thesis for the chemistry major on the topic of barium stability in pottery glazes.
References

