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Investigation of the Pattern and Composition of the Mysterious Dzi Beads using Advanced Spectroscopy and Imaging Techniques

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The origin of Tibetan Dzi beads has always been a mystery. The people of Tibet worship these beads for their presumed positive spiritual benefits. It is said that the wearer of a Dzi bead is protected from catastrophe, by warding off evil spirits that may pose negative effects.[1] There are many origin stories that tell of how these beads were formed - one well-known story talks about the Dzi beads originally as insects. The story recounts a man in the mountains who threw his hat over one of these insects. When he lifted his hat, he noticed that the insect had been petrified and turned into stone; and this object is said to have been a Dzi bead.[2]

My undergraduate thesis project in the T.K. Sham Group involves the characterization and imaging of a three-eyed Dzi bead (Figure 1). The three-eyed Dzi bead pattern is said to represent the three stars of luck: happiness, honour, and longevity.[2] These beads also come in many other shapes, sizes, and patterns, each with their own unique meaning. The demand for Dzi beads has increased in Asian countries due to their believed spiritual properties and therefore, has spurred the production of replicas. Thus, the objective of this project is to identify if the bead pattern is natural or manufactured, as well as identifying if the bead itself is genuine or a replica.

Various spectroscopic and imaging techniques have been used to observe the characteristics of the Dzi bead, in the hopes that they will reveal information about the origin, composition, and distribution of the bead. The results thus far have revealed the bead's composition be primarily silicon dioxide. In the Nanofabrication Facility; Optical Microscope, Scanning Electron Microscope (SEM), and Energy-Dispersive X-Ray Spectroscopy (EDX) have been used. These techniques were used to observe any deviations of the bead's surface that may give evidence regarding the formation of the three-eyed pattern. The images obtained have revealed an interesting set of circular etched or weathered rings that cover the surface of the bead in a random pattern (Figure 2, 3). They appear all over the bead's surface, regardless of the area being the light or dark part of the pattern. These rings are of interest as they may show evidence of the bead's age and origin and will continue to be studied further.

I would like to give a special thank you to both Tim Goldhawk and Todd Simpson for all their help in the Nanofabrication Facility.

Figure 1: Dzi bead used for this project

Figure 2: Microscope image showing an etched ring that appears on the surface

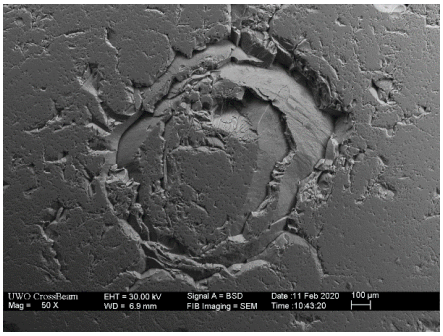

Figure 3: SEM image showing a second etched ring on the surface

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2. The Myth and Mystery of Tibetan Dzi Stone Beads. https://owlcation.com/social-sciences/The-Myth-and-Mystery-of- Tibetan-Dzi-Stone-Beads.

Icelandic Dust: Geophysical Characteristics Affecting Entrainment and Deposition

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Dust in high latitude cold climate (hlcc) regions, such as Iceland, is not well studied in comparison to dust in dry, hot desert regions. Icelandic dust regions are rapidly expanding with the exposure of new dust sources created from glacial melting (Bullard et al., 2016; Bullard, 2013) and catastrophic volcanic eruptions (Thorsteinsson et al., 2012). It is widely speculated that the characteristics of the particles influence their susceptibility to entrainment, emission, transport, and deposition, yet we have few in-situ measurements to test this hypothesis and serve as model input parameters. There is a need for better parameterization of these particles in atmospheric and climate models (Wiegner et al., 2012; Leadbetter et al., 2012; Johnson et al., 2012), which lack direct information about the particle characteristics and assume that the particles are close to solid spheres. Hence, this study aimed to understand and quantify the physical and mineralogical characteristics of Icelandic dust.

Three samples collected within and near regions of severe erosion located in southern (2010 Eyjafjallajökull Ash and glaciogenic sediments) and northeast (glaciogenic sediments) Iceland were used in this study. Each sample contained large amounts of silt and was wet-sieved to isolate only fine particles ≤ 50 µm. The Horiba-Partica LA-950 V2 PSA was used to measure their size distribution. Scanning electron microscopic (SEM) images of 2500 particles within each sample were analyzed to quantify their sphericity, surface area, and diameter, using Matlab image processing software. A focused ion beam (FIB-SEM) was used to mill miniscule particles in order to obtain high-resolution micrographs of their internal pore structure. A helium pycnometer was used to measure the particle density. The Brunauer, Emmett and Teller (BET) Gemini VII 2390 surface area and porosity analyzer was used to determine the specific surface area of the fine particles to assess complexities such as coatings, cracks, grooves, pores and cavities (Brunauer, 1945). X-ray diffraction (XRD) was used to identify the mineralogy of the three wet-sieved samples.

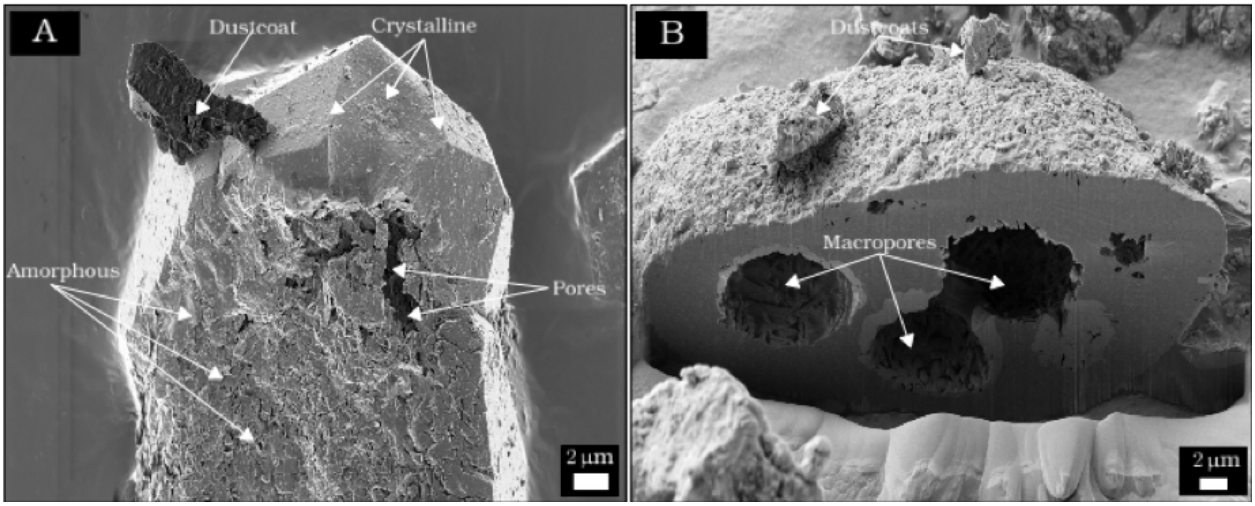

Figure 1: a) Typical features of a Glaciogenic particle collected in southern Iceland and b) Focus ion beam scanning electron microscopic (FIB-SEM) images of the internal structure of a 65µm Eyjafjallajökull Ash particle after FIB milling.

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The ultrafine Icelandic dust particles contain surface pores as well as large internal pores, large amounts of glass, and a significant quantity of nanosize dust coats (Figure 1a). The high porosity significantly alters the particle density, while the variability in mineralogy has little effect. The results showed that the pore sizes also appear to increase with particle size, reducing particle density. An abundance of volcanic glass also seems to increase the porosity and roughness and is strongly related to the BET surface areas. A focus ion beam scanning electron microscopic (FIB-SEM) images captures the internal macropores near the center of the cross section of a 65 µm Eyjafjallajökull Ash particle after FIB milling, and fewer fine, irregular-shaped pores (Figure 1b).

This study has shown that ash particles have complex surface structures. They are highly porous, and the effects of porosity significantly reduce their density. Therefore, model parameterization must be developed to incorporate these complexities to improve the prediction of dust emission processes.

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Wiegner, M., Gasteiger, J., Groß, S., Schnell, F., Freudenthaler, V., and Forkel, R., (2012). Characterization of the Eyjafjallajökull ash-plume: Potential of lidar remote sensing. Physics and Chemistry of the Earth, Parts A/B/C, 45, 79-86.

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Multifunctional Poly(Vinyl Alcohol) Hydrogel Beads for Transarterial Chemoembolization

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Transarterial chemoembolization (TACE) is the most common palliative treatment for patients with inoperable hepatocellular carcinoma (HCC) [1].

Current TACE technique uses drug delivery systems composed of drug-incorporated biostable microspheres to act as both an embolic agent to block the blood vessels and a drug depot to carry drugs to tumor sites [2]. As a result of this, tumor cells are killed due to the therapeutic effect of the drug and the ischemic necrosis induced by embolization. Microbead systems confine the drug within the tumor sites, and therefore reduce the toxic effect to healthy tissues [3]. To visualize the delivery, image contrast agents are administered independently.

The purpose of this study is to develop a micrometer size delivery package that can achieve all desirable functions at the same time. Polyvinyl alcohol (PVA), a biocompatible and biostable polymer is used as the matrix for the delivery system. PVA microparticles within a size range suitable for plugging blood vessels are fabricated using a custom designed microfluidic device. Two types of nanosized particles, silica nanoparticles (SiNPs) and superparamagnetic iron oxide nanoparticles (IONPs), are incorporated into the microparticles to immobilize drugs, enhance image contrast and enable degradation/dissolution of the deliver package. The nano-on-micro delivery system makes sustained drug release, visualization and repeated treatments possible.

The scanning electron microscope (SEM) at the Western Nanofabrication facility allows us to visualize microbeads as well as acquire elemental information of the products. Figure 1A illustrates an intermediate product of SiNPs formed in the presence of PVA. Figure 1B shows the morphology of a PVA-SiNP-IONP microbead.

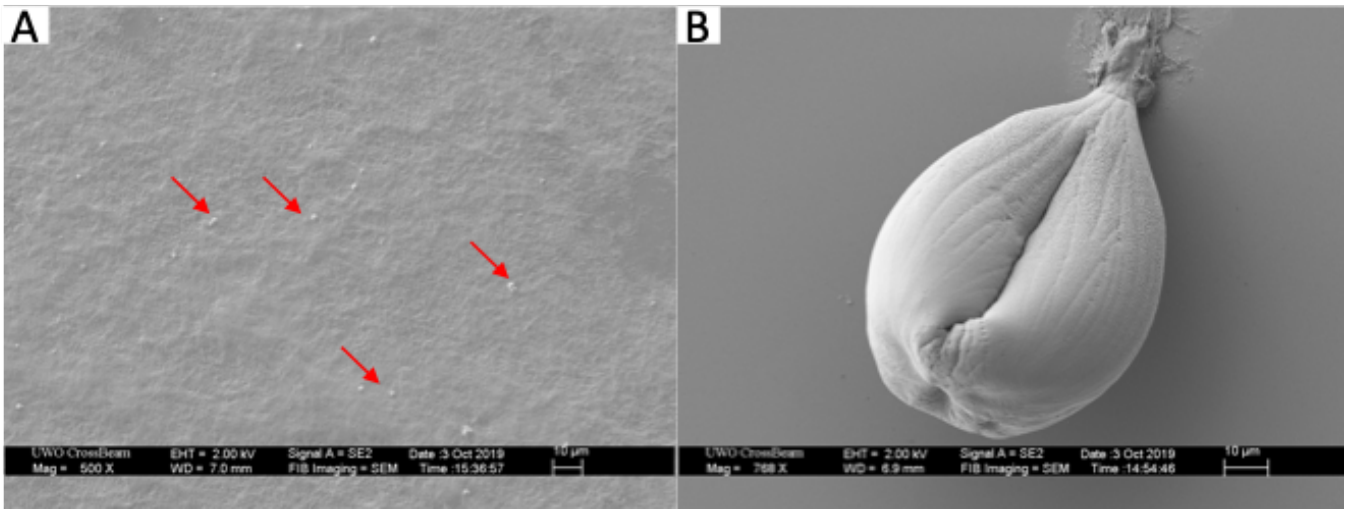

Figure 1. (A) SEM image of PVA-SiNP nanocomposite gel (red arrow pointing towards SiNPs). (B) SEM image of a PVA-SiNP-IONP microbead (before performing any freeze-thaw cycles).

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Its porous and 3-D structure are highly desirable in drug loading and controlled release. In addition, the energy dispersive X-Ray (EDX) spectroscopy identifies principle components and confirms the co-existence of SiNPs and IONPs in the PVA matrix of the microbeads (Figure 2). The EDX mapping further reveals the uniform distribution of nanoparticles throughout the microbeads.

We have successfully fabricated microbeads with an equivalent spherical diameter of 95 22µm. These beads possessed superparamagnetic property and provided contrast enhancement to T_2 weighted magnetic resonance (MR) images. An anti-tumor drug Doxorubicin was successfully incorporated in the beads (79.5 mg/g loading), and its release was studied in phosphate-buffered saline (PBS) at varying pH at 37 °C. These microbeads can provide a cumulative release of 27% in 70 days and they degrade over time as a function of pH.

In the next phase of this project, we will study tumor cell response to Doxorubicin released from the microbeads. We believe this multifunctional nano-on-micro delivery system has great potential to advance the current TACE therapy to be more effective.

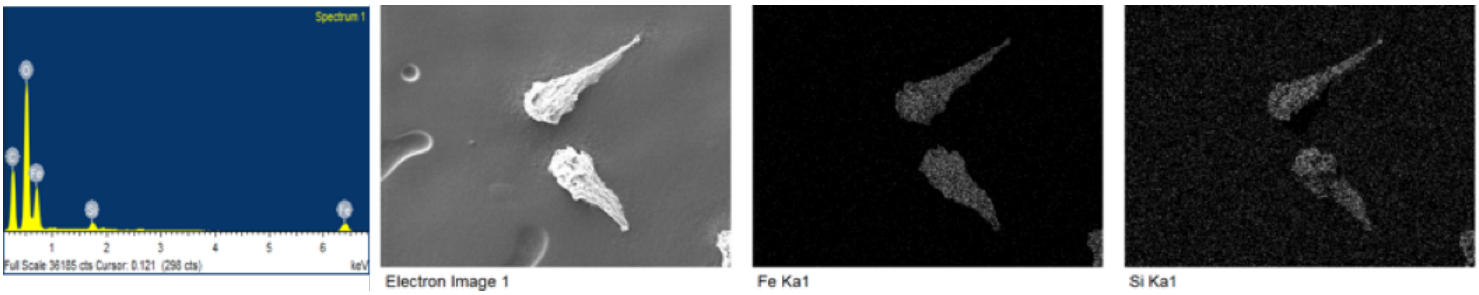

Figure 2: Elemental analysis and EDX mapping confirming the coexistence of SiNPs and IONPs in the PVA-SiNP-IONP beads.

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