AQUEOUS SURFACE CHEMISTRY OF DIAMOND GRAINS. A. W. Phelps, University of Dayton Research Institute, 300 College Park, Dayton, OH, 45469-0130, phelps@saber.udayton.edu.

Introduction Some diamond grains extracted from meteorites and chondritic porous (CP) aggregates are believed to have survived since before the formation of the solar system (Lewis et al., 1987; Anders and Zimmer, 1993; and Ott, 1993). Interstellar diamond is chemically extracted from meteoritic and chondritic porous host material as the first step in preparing the material for isotopic analysis. The Murchison K process (Amari et al., 1994) relies heavily on wet chemical oxidative steps to remove all non-diamond carbon from a concentrate. However, diamond is not inert to attack by the oxidizing agents used in this process and skewed results will be obtained if current grain processing methods destroy even a small amount of diamond. The very small size of interstellar diamond grains makes them particularly sensitive to oxidative attack due to their large surface to volume ratio. The work to be reported will examine the surface chemistry of both synthetic and natural nanodiamonds.

Background In order to develop more benign methods of extraction and improved recovery yields, the surface chemistry of the diamond grains must be taken into account. Natural diamond found in unaltered kimberlite (blue ground) is hydrophobic while diamond in hydrothermally altered kimberlite (yellow ground) and in alluvial deposits tends to be hydrophilic. In fact, hydrophilic diamond must be altered to hydrophobic in order to be processed in the same manner as other diamonds. Freshly cleaved diamond surfaces are also hydrophobic. Interactions of diamond surfaces with gases and liquids have been examined by a number of groups (Hartley and Shergold, 1993; Kuznetsov et al., 1991; Martynova and Nikitin, 1988; Pate, 1986; Pehrsson et al., 1994; Sappok and Boehm, 1968). Chemisorbed hydroxyl is believed to be responsible for the hydrophobic character of fresh diamond surfaces. Hydrogen has been shown to desorb only at high temperatures (>900°C) in vacuum but is easily replaced by oxygen containing species in aqueous solution. Hydrophobic diamond which has been aged in water or oxidizing acids will become hydrophilic and have a surface saturated with a variety of oxygen containing surface groups.

Fig. 1. Electrophoretic mobility (µm s⁻¹ V⁻¹ cm⁻¹) versus pH for fresh diamond powder (top) and diamond powder aged in water for 14 days (bottom). Adapted from Hartley and Shergold, 1993.

Figure 1 shows that the isoelectric point for fresh diamond is pH 3.5 and much less for water aged (oxidized) diamond. The surface charge on the aged diamond is negative due to the presence of hydroxyl. This fresh diamond was natural diamond with metallic contaminants and had significant amounts of silicon and zirconium impurities (0.5%).

Discussion The surface chemistry and reactivity of diamond powder will be a strong function of the crystallographic structure, particle size and morphology, and surface area. Lewis et al. (1989) state that the grains they measured had “an excellent fit to a log normal distribution with a median diameter of 26 Å”. Small particles tend to be very chemically reactive as the square-cubed relationship between surface area and volume becomes large at very small radii. The outermost layer of atoms will reorder and stretch their bonds to the next atomic layer down. This is not a problem with large samples but the next layer down for extremely small grains may represent a significant portion of the total volume.

The crystal structure of the grains will be an important factor in the chemical reactivity of the surface. Spear et al. (1990) and Phelps et al. (1993) review the structures of cubic diamond and the other hexagonal and rhombohedral polytypes of diamond including lonsdaleite (2H diamond). The diamond polytypes are characterized by the stacking arrangement of their carbon layers. Cubic diamond (3C) is related to zincblende (ZnS) and beta (SiC) cubic phases.

Fig. 2. The relationship between stacking arrangements in cubic diamond and lonsdaleite along the (111) and c-axis directions respectively.

The chemical reactivity of these two different structures will be very different at very small sizes. The number of re-entrant bonds present in the various stacking arrangements will become a dominant factor in the oxidation of these grains. The degree of hexagonal character of the polytype will also control the polarity of the of the diamond surface and so alter the dielectric constant (ionicity etc.). Daulton et al (1996) demonstrate that there is an admixture of hexagonal diamond in interstellar diamond extracted from meteorites.
Gentler methods of powder separation are necessary which do not damage the as-formed diamond grains. Likewise, a method which does not alter the surface chemistry of the diamond grains is desirable - thus allowing direct comparison of the surface chemistry of the meteoritic diamond with the synthetic diamond.

This work will examine and compare the surface chemistry of synthetic and natural nano-diamonds. The synthetic nano-diamonds will be prepared in a CVD flowing stream system and the natural diamonds will be separated from kimberlite and lamproite host rock.

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