Inkjet printing and nanoindentation of porous alumina multilayers

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**Abstract**

The objectives of this study were to analyse the effect of inkjet 3-D printing parameters, particularly the split overlap distance, for the fabrication of defect-free porous Al₂O₃ ceramic multilayers, and to correlate the resulting porosities with the mechanical properties measured using nanoindentation. An aqueous-based alumina ink was used in this study to fabricate the multilayers on dense alumina substrates by inkjet printing. The as-printed specimens were dried and sintered at 1200–1500 °C. The resulting microstructural features of each specimen and their corresponding porosities were studied using FIB-SEM. Elastic modulus and hardness were determined using the spherical nanoindentation technique. Results showed that defect-free porous alumina multilayers with excellent layer to layer and layer to substrate integrity were successfully fabricated. The porosity-dependence of the elastic modulus and hardness was shown to be consistent with values predicted using empirical expressions, despite the presence of abnormal grain growth at higher temperatures.

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**1. Introduction**

Porous ceramic materials possess many attractive properties compared to their dense counterparts, such as high permeability, high specific surface area, low thermal conductivity, and low density. They are widely used in applications as filters, sensors, catalyst supports, lightweight structural components, bioreactors, bone substitute, thermal insulators and heat exchangers [1–7]. Essential mechanical properties such as elastic modulus, hardness and fracture strength are associated with deformation behaviour when subject to mechanical loading are critical to understand for many of these applications. Porous ceramics are usually characterised by mechanical properties that are much inferior to their dense counterparts, and thus are vulnerable to damage. The mechanical properties of porous ceramics are mainly controlled by their microstructural characteristics such as porosity, pore structure and particle bonding. Therefore, understanding the relationship between the mechanical properties and the microstructural characteristics of the porous ceramics is an important step to help improve their reliability and durability in practical applications.

Inkjet 3-D printing [8] – one of the most promising contactless additive manufacturing methods – has attracted significant attention due to its cost-effective and direct additive building process for the formation of submillimeter-scaled and multi-material components. The incremental building process involves the on-demand ejection of fine droplets from a suspension loaded with material particles over the required locations by the mechanically controlled positioning of the print-head. The deposited layers of droplets are then dried through solvent evaporation before repeating the building of the next layer. The technique has been widely applied in the printing of engineering ceramic objects using a wide range of materials [9–11], including microstructured pillars [12], delicate electronic components [13], multifunctional sensors [14], refractive optical components [15] and fuel cell electrodes [16].

In the literature, there are only a few studies reported on the inkjet printing of alumina components [17–20]. Most work has focused on the ink preparation and optimisation and printing performance of the print heads. On the other hand, many studies have reported the mechanical characterisation of partially sintered porous alumina microstructures prepared using conventional processing methods, such as die-pressing [21,22], slip-casting [23] and extrusion [24]. However, no work has yet been reported on the measurements of the mechanical properties of alumina components fabricated by inkjet printing. Besides the characteristics of the ink, the print head and the substrate, the interaction of droplets and the drying and sintering processes also play essential roles in determining the quality, accuracy and properties of printed components. But there has been little systematic work on these aspects of ceramic processing by inkjet printing in the literature [25].

The present study focuses on the fabrication of porous Al₂O₃ ceramic multilayers using an inkjet 3-D printing technique and a...
water-based alumina ink. The main parameter affecting the continuity and integrity of the printed layer – the splat overlap distance, was first investigated. Optimised values were found for obtaining gap-free single layers. The relationship between the sintering temperature and the resulting microstructure and porosity of the porous sintered specimens, was studied using a Focused Ion Beam-Scanning Electron Microscope (FIB-SEM). The elastic modulus and hardness of the as-sintered specimens were determined using the nanoindentation technique [26], with only small amounts of material required. The influence of the porosity on the elastic modulus and hardness were discussed through comparison between the measured values and empirically predicted ones.

2. Experimental and simulation procedures

2.1. Inkjet 3-D Printing of alumina multilayers

An aqua-based Al2O3 ink provided by Ceradrop was used to fabricate the alumina multilayers via a Ceraprinter X-serie inkjet printing machine (Ceradrop, France). A Fuji Dimatix serie Sapphire QS-256/30 AAA multi-nozzle print head (Fujifilm Dimatix, USA), consisting of a line of 256 piezo-controlled nozzles arranged at 100 dots-per-inch spacing with 30 picoliter minimum drop size, was used. Prior to the printing process, the voltage and waveform applied to the print head were adjusted for the alumina ink to reach a consistent tail-free droplet ejection. This was realised by stroboscopic analysis of real time backlit images of the formation and ejection of droplets captured by a charge-coupled device (CCD) camera.

Commercially available as-sintered dense alumina plates (1 mm thick) were used as substrates on which printing was performed. Substrates of the same material as the solid content of the ink were used to minimise stress, and associated damage to the film, induced by any thermal expansion mismatch during cooling. Important ink properties and the initial inkjet printing parameters are listed in Tables 1 and 2, respectively.

The printing pattern used in this study was a squared lattice, shown in Fig. 1 as a schematic of four droplets jetted onto the substrate in each case, with the splat diameter being d, the axial overlap distance c and the diagonal overlap distance b. A simple linear relation exists between c and b, as shown below.

\[ c = \frac{b + d}{\sqrt{2}} - d \]  

(1)

The values of c and b can be either positive (Fig. 1(a)) or negative (Fig. 1(d)). A positive value means the adjacent splats are distanced along the relevant direction, whereas a negative value results in an overlap between them. Usually d is a fixed value when other working parameters are defined, b can be directly specified in the machine and can be varied to optimise the as-printed layer properties, i.e. mainly the integrity and thickness. Too much overlap would result in accumulative asperities in the as-printed specimen, whereas if significant gaps exist between splats the continuity of the as-printed specimen is in question so that the integrity is affected. Therefore, depending on the ink used, an optimum overlap condition (i.e. no gaps exist, as shown in Fig. 1(c)) can be found. Theoretically it is easy to deduce from Eq. (1) that when \( b = 0 \), \( c = -0.293d \). However, the experimental measurement, and hence the optimised experimental values, might be different due to drying after printing and the imperfect round-shape of the splats. To estimate such an overlap condition in the current case, square-shaped (1 cm x 1 cm) specimens were then printed with different numbers of layers (1–12), using an X–Y alternate printing order (i.e. the first layer printed along X-axis, then the second layer along Y-axis and repeated).

2.2. Drying and sintering

There are two stages of drying after printing: (1) a period of 2 min air drying is used after printing each individual layer, so that the structure has enough strength to support the next layer; (2) after the whole printing process is completed, the as-printed specimens were oven dried at 100 °C for 24 h before sintering at high temperatures. After oven drying, the average layer thickness obtained was measured to be approximately 10 μm. Sintering was carried out in air at elevated temperatures ranging from 1200 to 1500 °C. The rate of temperature change was set to be 10 °C/min during heating and cooling. A slower heating rate of 5 °C/min was set at the initial debinding stage from room temperature to 400 °C, to burn out the organic content in the green specimens while conserving their integrity. Holding periods of 2 h and 4 h were set at 400 °C and at the peak temperature, respectively.

2.3. Microstructural characterisation and porosity measurement

The specimens in both as-printed and as-sintered forms were studied using optical microscopy. The FIB-SEM slice and view technique was also used to further examine the surface and cross-sectional microstructural features. The average grain size was estimated based on the surface micrographs and the thickness of the multilayers were determined by examining the fractured cross-sections. The porosity was measured based on the 3D reconstructed microstructures using FIB tomography [27].

2.4. Spherical nanoindentation for mechanical property measurements

The instrumented nanoindentation measurements at loads ranging from 10 to 500 mN using a spherical diamond indenter of 25 μm radius were conducted on the as-sintered alumina specimens without further surface treatment (such as polishing). It was found in our previous study [27] that porous ceramic indentation with a spherical tip is more capable of reproducible measurements compared with a sharp tip.

The elastic modulus, \( E \), and the indentation hardness, \( H \), were calculated based on the load–displacement curves (Fig. 2) using the Oliver–Pharr analysis [26].

\[
H = \frac{P_{\text{max}}}{\pi a_{\text{c}}^2} \left( 1 - \frac{C}{Y} \right)
\]

(2)

where \( P_{\text{max}} \) is the maximum load applied and \( a_{\text{c}} \) is the contact area radius at maximum load and is given by \( a_{\text{c}} = \sqrt{2R_l h_c - R_l^2} \), where \( R_l \) is the indenter radius (\( = 25 \mu m \) here), \( h_c \) is the contact depth and...
was deduced using the relation \( h_c = \frac{h_{\text{max}}}{C_0^{0.75}} \frac{P_{\text{max}}}{S} \), with \( S \) being the contact stiffness calculated as the slope of the initial unloading curve at maximum load, \( E \) is related to the reduced modulus \( E_r \), by the following expression,

\[
E_r = \frac{1 - \nu^2}{E} \left( 1 - \frac{\nu^2}{E_i} \right)
\]

where \( E_r = S/2a_m \) and \( \nu \) is the Poisson’s ratio of the specimen, \( E \) and \( \nu_i \) are the elastic modulus and Poisson’s ratio for the indenter, respectively.

3. Results and discussion

3.1. Microstructure after drying and sintering

3.1.1. Effect of splat overlap distance on the integrity of printed alumina multilayers

In this study, very large values of the overlap distance parameters \( c = 33.2 \) and \( b = 80 \mu m \) were first used so that no overlap took place, and the single splat diameter could therefore be measured after drying, as shown in Fig. 3. The splat diameter was measured to be approximately \( 80 \pm 11 \mu m \), though the printed

![Fig. 1. Schematic of the printed splat layout using a squared lattice pattern with different overlap values. (a) \( b > 0 \) and \( c > 0 \), (b) \( b > 0 \) and \( c = 0 \), (c) \( b = 0 \) and \( c < 0 \), and (d) \( b < 0 \) and \( c < 0 \).](image1)

![Fig. 2. (a) Schematic of indentation process and geometries, (b) the resulting indentation load–displacement curve.](image2)

![Fig. 3. Study of the splat diameter and overlap distance parameters of printed patterns using optical microscope, with different magnifications (here \( b = 80 \) and \( c = 33.2 \mu m \) were used).](image3)
splits were not of a fully uniform and circular shape.

Since the theoretical optimum overlap values must be \( b = 0 \) and \( c = -23.4 \, \mu m \), the following range of \( b \) and \( c \) values (Table 3) were used to optimise the layer integrity based on Eq. (1).

The optical micrographs of the experimental printing results are shown in Fig. 4. It can be seen that the gap decreased as \( b \) was reduced. However, even when the theoretical values were reached (i.e. Fig. 4(e) with \( b = 0 \) and \( c = -23.4 \, \mu m \)), some gaps are still visible that affect the continuity of the printed specimen. When \( b \) was reduced to \(-10 \, \mu m \), no gaps were identified. Too much overlap was created when \( b \) was further reduced. Consequently, accumulative asperities were generated in the as-printed specimens - a significantly rougher surface is evident, particularly in Fig. 4(h) when overlap distance parameters \( b = -10 \) and \( c = -37.6 \, \mu m \) were used. On the basis of the above observations and analysis, \( b = -10 \) and \( c = -30.5 \, \mu m \) were selected as the optimum parameters for printing.

### Table 3: Splat overlap distance parameters \( a \) and \( b \) used in the study.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
<th>( e )</th>
<th>( f )</th>
<th>( g )</th>
<th>( h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b (\mu m) )</td>
<td>60</td>
<td>40</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>-10</td>
<td>-15</td>
<td>-20</td>
</tr>
<tr>
<td>( c (\mu m) )</td>
<td>18.9</td>
<td>4.9</td>
<td>-9.3</td>
<td>-16.4</td>
<td>-23.4</td>
<td>-30.5</td>
<td>-34</td>
<td>-37.6</td>
</tr>
</tbody>
</table>

3.1.2. The grain size and thickness of the as-sintered specimens

Specimens with 10 layers printed in an X-Y alternate order were prepared and sintered at 1200–1500 °C. The as-sintered specimens were investigated using FIB-SEM to see the surface and cross-sectional microstructures and to measure the grain size and thickness. The surface and cross-sectional micrographs are shown in Figs. 5 and 6, respectively.

It is evident in Figs. 5 and 6 that no detectable micro-cracking can be found in these specimens. It is also worth noticing that homogeneous microstructures were obtained for specimens sintered at 1200 and 1300 °C, while for those sintered at higher temperatures, a great number of significantly coarse (≈100 \( \mu m \)) grains were formed. The presence of such grains was due to the abnormal grain growth (AGG) behaviour, frequently occurring in alumina sintering [28–31]. AGG in alumina can be associated with many factors, such as sintering temperature, sintering conditions and material purity [31]. Besides the high temperatures of 1400 and 1500 °C allowing AGG to take place in this study, another critical factor is most likely to be the level of impurities, in both the ink’s solid content and the substrate. Studies have considered the presence of glassy phase impurities such as Na, K, Ca and Si in alumina powder the primary cause of AGG [31,32]. Some alumina may contain typically 2–4 wt% glassy phase. This lowers the sintering temperature and promotes grain growth. Although doping with a few hundred ppm of MgO have been proved to effectively prevent AGG behaviour in alumina [33–35], the subtle modification of the ink and substrate compositions is beyond the scope of this study.

Fig. 6 also shows that a flat surface was obtained for all specimens, suitable for nanoindentation measurements. Furthermore, no delamination of the layers from the substrates was detected – indeed as the sintering temperature increased, the abnormally grown grains connected to the substrate particles. Notwithstanding that each specimen was printed with 10 layers on top of the substrate, excellent layer to layer bonding after sintering is evident in Fig. 6, as no visible layer boundaries can be identified in the figures. This further demonstrates the homogeneity of the microstructures, particularly for the specimens sintered at 1200 and 1300 °C before the abnormally large grains were formed when sintering at even higher temperatures. The higher magnification images Fig. 6(f) and (h) also show the very small closed pores inside the large grains, circled by the red dashed ovals.

Table 4 lists the measured average grain size, larger grain size and thickness of the specimens, along with the standard deviation. Note that for the specimens sintered at 1400 and 1500 °C, the average grain size measures the size of the grains excluding the abnormally grown grains with much larger size. The average size of the abnormally grown grains measures the length and width of the quasi-rectangular shape based on the top surface micrographs taken. The grain size increased 10 times as the sintering temperature increased from 1200 to 1500 °C, while the specimen thickness was largely reduced from 82 \( \mu m \) to 36 \( \mu m \). The larger standard deviation of the average grain size for the specimens sintered at 1400 and 1500 °C indicates greater inhomogeneity of the corresponding microstructures, compared with those sintered at lower temperatures.

### Table 4: Average grain size, larger grain size and thickness of the specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
<th>( e )</th>
<th>( f )</th>
<th>( g )</th>
<th>( h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b (\mu m) )</td>
<td>23.4</td>
<td>16.4</td>
<td>-23.4</td>
<td>-30.5</td>
<td>-34</td>
<td>-37.6</td>
<td></td>
</tr>
<tr>
<td>( c (\mu m) )</td>
<td>30.5</td>
<td>18.9</td>
<td>4.9</td>
<td>40</td>
<td>-10</td>
<td>-15</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Mechanical property measurements using nanoindentation

3.2.1. Elastic modulus (\( E \)) and hardness (\( H \)) determination

Nanoindentation measurements at a range of indentation loads/depths were carried out for these specimens sintered at different temperatures. As the specimens in the present study are porous microstructures and various effects can take place, notably

Fig. 4. Comparison of single layer surface morphologies with different overlap distance parameters after drying (a) \( b = 60 \) and \( c = 18.9 \, \mu m \), (b) \( b = 40 \) and \( c = 4.9 \, \mu m \), (c) \( b = 20 \) and \( c = 9.3 \, \mu m \), (d) \( b = 10 \) and \( c = 16.4 \, \mu m \), (e) \( b = 0 \) and \( c = 23.4 \, \mu m \), (f) \( b = 10 \) and \( c = 30.5 \, \mu m \), (g) \( b = 15 \) and \( c = 34 \, \mu m \), (h) \( b = 20 \) and \( c = 37.6 \, \mu m \).
the densification of microstructure, surface roughness and substrate effects. The common experimental practice is that indentation depth should be less than 1/10 of the specimen thickness so that the effective film mechanical properties can be reliably determined. In this study, nanoindentation tests were carried out at loads ranging from 10 to 500 mN, resulting in maximum indentation depths of 0.8–6 μm, well below 1/10 of each corresponding multilayer thickness. The calculated elastic modulus and indentation hardness are plotted as a function of indentation depth, as shown in Fig. 7, for each specimen sintered at different temperatures. The features of the plots also reflect the microstructural observations described earlier. For the specimens sintered at 1200 and 1300 °C, plateau moduli and hardness are quickly attained as the indentation depth increases, due to the uniform microstructures generated. The large deviation at low indentation depths is most possibly attributed to the slight surface roughness of the specimen surfaces. In contrast, for the specimens sintered at the higher temperatures of 1400 and 1500 °C, significantly larger deviations take place for all indentation depths due to the relatively larger surface roughness as a result of the

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Fig. 5. Comparison of surface micrographs of the specimens sintered at (a) 1200 °C, (b) 1300 °C, (c-d) 1400 °C and (e-f) 1500 °C. Note the scales are different in each case.
Fig. 6. Comparison of cross-sectional micrographs of the specimens sintered at (a–b) 1200 °C, (c–d) 1300 °C, (e–f) 1400 °C and (g–h) 1500 °C. Note the different scales in each case.
abnormal grain growth, as shown in Fig. 6, compared with the size of the indenter. Furthermore, the abnormally grown large grains lead to inhomogeneity of the microstructure responsible for the lack of well-defined plateau values. There is no further increase of $E$ or $H$ after large indentation depth is reached, suggesting an almost negligible effect from densification of the porous microstructure.

3.2.2. Porosity dependence of elastic modulus and hardness

The effective elastic modulus and hardness can be estimated based on the above plots and the values are shown in Table 5. Also tabulated are the values of porosity measured based on FIB-SEM tomography. It is clear that both the elastic modulus and hardness increase dramatically when the porosity decreases. It is worth noting that the specimen experienced significant densification, and hence a large drop of porosity, when the sintering temperature was increased from 1300 to 1400 °C.

Table 4
Measured grain size and thickness of the as-sintered specimens.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average grain size (nm)</td>
<td>134 ± 32</td>
<td>241 ± 43</td>
<td>468 ± 131</td>
<td>1532 ± 801</td>
</tr>
<tr>
<td>Average large grain size (μm)</td>
<td>N/A</td>
<td>N/A</td>
<td>(69 ± 15) × (10 ± 2)</td>
<td>(99 ± 15) × (14 ± 3)</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>82 ± 1</td>
<td>54 ± 2</td>
<td>38 ± 3</td>
<td>36 ± 5</td>
</tr>
</tbody>
</table>

Table 5
Mechanical properties and porosities of the sintered specimens.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Porosity $p$</th>
<th>Elastic modulus $E$ (GPa)</th>
<th>Indentation hardness $H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>0.57</td>
<td>45</td>
<td>0.61</td>
</tr>
<tr>
<td>1300</td>
<td>0.41</td>
<td>92</td>
<td>1.46</td>
</tr>
<tr>
<td>1400</td>
<td>0.17</td>
<td>229</td>
<td>4.96</td>
</tr>
<tr>
<td>1500</td>
<td>0.14</td>
<td>250</td>
<td>6.57</td>
</tr>
</tbody>
</table>

There are many empirical equations reported regarding the relationships between porosity and mechanical properties, particularly the elastic modulus, of partially sintered ceramics [36,37]. Among them, the most widely used ones are the one proposed by Ramakrishnan and Arunachalam [38] (composite sphere method) for solids with randomly distributed pores, and the one proposed by Spriggs [39], as expressed by Eqs. (4) and (5), might be able to describe the porosity dependence of the specimens in the current study.

$$E = E_0 (1-p)^2 \left(1 + \rho_{\text{L}} \rho_{\text{E}} \right)$$  \hspace{1cm} (4)

$$E = E_0 e^{-\rho}$$  \hspace{1cm} (5)

where $E_0$ is the elastic modulus of fully dense material, $p$ is the...
pore volume fraction, \( m_E \) is a parameter depending on Poisson’s ratio \( v_0 \) of fully dense material, with \( m_E = 2 - 3v_0 \), and \( n \) is an empirical constant, and can be deduced by fitting the relationship \( \ln(E) = -np + \ln(E_0) \) to experimental results, as shown in Fig. 8(a). In this study, \( E_0 \) and \( v_0 \) are assumed to be 400 GPa and 0.22 [40], respectively. As a result, the calculated \( n \) equals 3.97, which is almost the same as that reported by Knudsen [41]. Both the empirical expressions are plotted as a function of porosity to compare with the experimental results found in the current study in Fig. 8(b). The data compare well with the empirical prediction.

In the same way, the hardness as a function of porosity was also fitted using an exponential relationship \( H = H_0 e^{-kp} \), \( H_0 \) and \( k \) were obtained by fitting the expression to the experimental data, as shown in Fig. 9. The result shows a very satisfactory fitting with \( H_0 \) and \( k \) calculated to be 13.2 and 5.4, respectively. In summary, the elastic modulus and hardness of the inkjet printed porous alumina multilayers possessing a wide range of porosities of 0.14–0.57 were found to be accurately predicted by the simple empirical relationships involving the degree of porosity as a variable.

4. Conclusions

In this paper, we study experimentally porous alumina multilayers which were inkjet 3-D printed and sintered at different temperatures of 1200–1500 °C, with resulting porosities ranging from 0.14 to 0.57. Spherical nanoindentation measurements were carried out and the microstructures were investigated using optical microscopy and the FIB-SEM slice and view technique.

Defect-free green specimens were successfully printed. The cross-sectional microstructure analysis revealed excellent layer to layer and layer to substrate integrity, partly attributed to the appropriately controlled drying and sintering processes. Relatively uniform microstructures were prepared after sintering at 1200 and 1300 °C, while higher sintering temperatures resulted in the abnormal growth of significantly large grains of sizes over 100 μm. The average (small) alumina grain size increased 10 times but was constrained at micron scale as the sintering temperature increased from 1200 to 1500 °C, while the specimen thickness reduced over half from 82 μm to 36 μm.

Mechanical properties, including the elastic modulus and hardness of the printed porous alumina multilayers, were measured using nanoindentation technique. The results show a load dependence of the measured elastic modulus and hardness, due to the surface roughness effect and the inhomogeneity of the microstructures when sintered at temperatures higher than 1400 °C. Elastic modulus and hardness data were found to experience a significant increase during sintering between 1300 and 1400 °C, as a result of the abnormal grain growth. Nevertheless, a range of plateau values can be assessed to estimate the effective mechanical properties based on the measured results as a function of indentation depth. As a result the estimated values of elastic modulus and hardness are 45–250 GPa and 0.61–6.57 GPa, respectively, with an increase by about factors of 5.6 and 10.8. The results show that the analysis by indentation can give a good estimate of the elastic modulus and indentation hardness of the porous alumina multilayers.

Based on the above results, the porosity–mechanical property relationships were further explored by applying previously reported simple empirical relationships (both polynomial and exponential) involving the degree of porosity. Although they do not have a strong fundamental basis, they were found to be very useful in predicting the elastic modulus and hardness data of the porous alumina multilayers as a function of porosity with excellent accuracy.
Acknowledgement

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Appendix A. Supplementary data

Raw data on which this paper is based can be openly accessed at http://dx.doi.org/10.6084/m9.figshare.2114344.v1.

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