



HAL
open science

Investigating the mechanisms of diamond polishing using Raman spectroscopy

Jonathan Hird, Matthew Bloomfield, Ian Hayward

► **To cite this version:**

Jonathan Hird, Matthew Bloomfield, Ian Hayward. Investigating the mechanisms of diamond polishing using Raman spectroscopy. *Philosophical Magazine*, 2006, 87 (02), pp.267-280. 10.1080/14786430600953772 . hal-00513765

HAL Id: hal-00513765

<https://hal.science/hal-00513765>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Investigating the mechanisms of diamond polishing using Raman spectroscopy

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-06-May-0136
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	02-May-2006
Complete List of Authors:	Hird, Jonathan; Cavendish Laboratory Bloomfield, Matthew; Renishaw plc, Spectroscopy Products Division Hayward, Ian; Renishaw plc, Spectroscopy Products Division
Keywords:	diamond, Raman spectroscopy, wear
Keywords (user supplied):	polishing, iron oxides



Investigating the mechanisms of diamond polishing using Raman spectroscopy

J. R. HIRD^{†*}, M. BLOOMFIELD[‡], I. P. HAYWARD[‡]

[†]Physics and Chemistry of Solids, Department of Physics, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, UK

[‡]Spectroscopy Products Division, Renishaw plc., Old Town, Wotton-under-Edge, Gloucestershire GL12 7DW, UK

Correspondence *Jonathan Hird. Email: jrh50@cam.ac.uk

Recent research has shown that a phase transformation of the diamond to a different form of carbon is involved when diamonds are polished in the traditional fashion. The question as to how this phase transformation is activated and maintained to produce high wear rates is of great technological interest since it may radically change the way we view the processing of diamond. This paper describes the use of Raman spectroscopy to examine debris produced on the diamond polishing wheel, both during its preparation and during polishing. In addition, polished diamond surfaces were examined for the possible existence of non-diamond surface layers in an attempt to identify material removal mechanisms. Raman spectroscopy proves ideal for these analyses because its relatively high spatial resolution is well suited to the analysis of small wear features and debris particles, and because of the wealth of information it reveals about chemical structure. This level of structural information has been lacking in previous analyses of diamond polishing debris. In addition to the non-diamond carbon found in the wear debris, significant quantities of two iron oxides – magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) were also found. An interesting observation was that a transformation from magnetite to hematite could be induced either by using high power laser excitation, or by frictional heating during polishing. It is suggested that some of the Raman peaks previously attributed to lonsdaleite might better be explained by the presence of these oxides.

Keywords: Diamond; Raman spectroscopy; polishing; wear; lonsdaleite; iron oxides.

1. Introduction

In the 85 years following the publication of the Tolkowsky's seminal work on the subject [1], at least three main ideas have dominated the literature into how a diamond – the hardest known substance – may be worn away and polished, following a technique honed by 600 years of practical use. Fracture, thermo-chemical and mechano-chemical based wear (and combinations thereof), have all variously been mooted as responsible for the removal of material from a diamond under polish.

Diamond polishing is perhaps an inappropriate name for this process since, when a skilled lapidary is at work, wear and polishing are carried out simultaneously. It is possible to solely induce wear to a diamond under certain conditions, but these are generally avoided as in this case the removal mechanism involves abrasive

1
2
3 wear and fracture, and is thus detrimental to single-crystal gemstones. Abrasive wear may be invoked using a
4 special kind of polishing wheel to cut ‘difficult’ stones (those exhibiting crystallographic defects), and is
5 usually the method of choice for initially lapping polycrystalline diamonds.
6

7 The research presented in this paper is concerned with the traditional polishing technique, whereby a diamond
8 is pressed against a rapidly rotating cast iron disc loaded with a mixture of diamond grit and oil. While the
9 anisotropy in wear has been known about for centuries by industry workers, it was only relatively recently
10 that it was given scientific attention [1]. The maximum wear-rate for all surfaces occurs in $\langle 001 \rangle$ (cube)
11 directions on $\{110\}$ (dodecahedral) surfaces. Directions of maximum wear are dubbed ‘soft’ in the trade and
12 it is in these directions of polish that wear and polishing takes place simultaneously to give a fine, mirror-like
13 finish. It is the mechanisms of wear under these conditions that this paper seeks to elucidate.
14
15

16 Investigations into the wear behaviour of most materials are relatively straightforward to perform but
17 interpretation is usually non-trivial [2]. This is due to the number of factors which may be involved, such as
18 material properties, phase transformations and the constantly changing contact conditions. All of these may
19 be a function of temperature, which in itself is usually indirectly related to the friction between the rubbing
20 surface and the velocity of polish. With diamond polishing, the problem is compounded by the complexity of
21 obtaining even basic wear measurements, due to the extreme hardness and wear resistance of diamond.
22 Typically, one obtains wear rates of a few tens of micrometres per minute, and this is challenging to measure
23 under standard industrial conditions. Furthermore, the diamond polishing wheels, or scaifes as they are more
24 commonly known, are not purchased ready prepared. Preparation is carried out in the workshop in which they
25 are to be used. Inevitably, experimental results on this subject are conflicting (see [3] for a thorough review),
26 though several recent papers have addressed these issues using a different approach [3, 4]. Diamonds are also
27 expensive and as a consequence reported research has been hampered by the lack of suitable specimens with
28 regular geometry, in the necessary quantities to render the work statistically valid.
29
30
31
32

33 Perhaps as a result of this, research on diamond wear has tended to branch into two main areas: low speed
34 frictional sliding experiments – measuring friction with controlled contact and atmospheric conditions [5–13]
35 and post-wear analysis which has included studies of the diamond surfaces after polishing and friction
36 experiments [14–17] and debris analysis [9, 11, 12, 18–21].
37
38

39 2. Post-wear analysis

40
41
42 Tolkowsky [1] believed that the wear mechanism for diamond was the removal of miniature diamond
43 tetrahedra and octahedral components from the bulk diamond. This was perhaps not surprising given that
44 abrasion on an ever decreasing scale (for a finer finish) was thought to be a polishing mechanism since the
45 time of Newton. Indeed, the French crystallographer, Haüy believed that the bulk of any crystal was made up
46 of smaller kernels of the same. Tolkowsky’s theories were not supported by visual observations, however,
47 and it is somewhat unfortunate that Tolkowsky dismissed the explosion of work being carried out at that time
48 on the formulation of modern physics as ‘...useless’ in relation to the understanding of diamond polishing.
49 He is, however, best remembered for the design of what is today known as the basis of the standard round
50 brilliant or Tolkowsky cut diamond. Despite his rather blinkered view of modern physics, micro-fracture has
51 been favoured by some as a valid removal mechanism up until it was shown to be highly improbable (in ‘soft’
52 polishing directions) by Couto *et al.* in the 1990s [21]. That micro-fracture was favoured by earlier authors
53 [22], is primarily due to the propensity of the diamond crystal to cleave along octahedral $\{111\}$ planes; it
54 being almost ideally brittle with the highest resistance to plastic deformation at room temperature of any
55 material. Unequivocal evidence exists showing that plastic deformation of diamond is achievable at elevated
56
57
58
59
60

1
2
3 temperatures [23, 24]. However, the case for plastic deformation at room temperature appears to be open to
4 interpretation (for a review see [25]).

5
6 Studies of diamond surfaces were performed as early as 1956 [14] and again in the 1970's [15] using electron
7 microscopy techniques but they failed to provide the resolution or contrast necessary to see the features
8 reported later by Couto *et al.* [21] who used scanning tunnelling microscopy (STM) and atomic force
9 microscopy (AFM). Couto found that diamonds polished in 'soft' directions exhibit smooth grooving on a
10 nanometer scale – grooves that appear to have been produced plastically rather than by any abrasive process.
11 'Polishing' in hard directions, however, result in surfaces which, when observed using AFM show a rough,
12 undulating surface structure consistent with being formed by a fracture-based process. The mechanism for the
13 removal of material in 'soft' directions remained elusive until recently, as plastic deformation in itself (if
14 indeed this is the mechanism of nano-groove formation) cannot be regarded as a removal mechanism. It does
15 appear, however, that plastic deformation is present as a direct consequence of another process. This is the
16 plane- or chisel-like action of the grit particles on a scribe which cause plastic flow on the surface of diamond
17 in a similar fashion to that produced on metals during conventional machining operations [3].

18
19 Analysis of diamond wear debris provides another approach to the problem and is attractive since samples can
20 be taken from numerous sources and analysed off-site. As such, many attempts have been made to understand
21 the nature and composition of wear debris from both friction and polishing experiments.

22
23 Analyses have variously included such techniques as infrared absorption (IR) spectroscopy [11, 21], energy
24 dispersive X-ray analysis (EDX) [9, 21], X-ray diffraction [11, 21], Raman spectroscopy [21] and various
25 forms of microscopy in conjunction with electron energy loss spectroscopy (EELS) [9, 12, 13, 19, 20],
26 electron diffraction [11] and analytical chemical tests [5, 11]. All analyses concluded that the result of
27 frictional sliding either during polishing or at low speed involving diamond-diamond contact is the formation
28 of non-diamond wear debris.

29
30 During low-speed atmospheric frictional sliding the debris is reported as having a waxy or greasy appearance
31 and its colour described as either fawn or a pale yellow. It is thought to be composed primarily of
32 hydrocarbons and/or amorphous carbon. Debris produced using similar sliding speeds *in vacuo* is darkly
33 coloured and contains fewer hydrocarbons suggesting a strong atmospheric dependence on the composition of
34 the debris [5, 11]. Trace levels of elements including Fe, Na, Cl, Si and Ca have also been found [9, 11]
35 although these are more likely to be contaminants rather than impurities in the diamond lattice. Analysis of
36 debris from the traditional polishing process has been reported to consist of amorphous or graphitic carbon
37 using EELS [19, 20] while Couto *et al.* [21] have additionally suggested (interpretation from visual
38 observations) that iron in the form of carbides and oxides may also be present – a likely result since the
39 polishing wheel is made from cast iron.
40
41
42
43
44

45 3. Wear mechanisms

46
47 It is clear that a proposed wear mechanism for diamond polishing must explain both the anisotropy and the
48 non-diamond wear debris. As mentioned earlier, chemical, mechanical, and thermal wear have all been
49 argued to play a part in the removal process. It is, however, becoming clear that a number of competing
50 processes may act, and that these are a function of the velocity of the sliding [3, 4]. It is also clear that
51 polishing on the scribe differs from low-speed frictional sliding due to the vastly different contact conditions,
52 the materials involved and the velocity of sliding; comparisons should thus be made with caution. Polishing
53 mechanisms are discussed here; for a review of the origins of diamond friction and associated wear debris the
54 reader is referred to [26].
55
56
57
58
59
60

1
2
3 The two most plausible mechanisms of wear during polishing considered to-date are thermally based [5] or
4 mechano-chemical [19, 27]. Thermal wear has previously been dismissed due to reports [22] that material
5 removal was linearly proportional to the abrading (NB: *not* polishing) velocity. These experiments were not
6 carried out under industrial polishing conditions, rather on miniature grinding wheels and more recent
7 research [3, 4, 17] challenges their view.

8
9 van Bouwelen *et al.* [27] suggest that a structural change due to the large shear stresses present at the
10 diamond-scaife interface is responsible for the non-diamond carbon wear debris. This mechanism is attractive
11 since it explains both the extraordinary tribological anisotropy and the associated wear debris, in terms of the
12 crystallographic structure of diamond.
13

14
15 Neither theory, however, has been proved beyond reasonable doubt and several problems are associated with
16 both. One question for both theories is what is the mechanism involved in the removal of the phase-
17 transformed material itself? Experimentally, it is possible for a lapidary to remove a diamond from a scaife
18 and for the surface to appear 'clean' and mirror-like even under an optical microscope. Given the oleophilic
19 nature of diamond surfaces and the (relatively) oily surface of a scaife, this is surprising. In contrast, a
20 diamond surface placed in an oven at temperatures high enough to produce graphitisation (usually *ca.* 600 K
21 in air) will show a blackened amorphous carbon surface. A thermal mechanism would have to explain this
22 discrepancy.
23

24
25 If on the other hand, a mechanically induced structural transformation *is* involved in the mechanism of
26 diamond polishing, it is reasonable to assume that an artefact of this might be observed on an as-polished
27 diamond surface consisting, for example, as a layer of non-diamond carbon.
28

29
30 Another possibility is that of thermo-chemical wear. Diamond is well-known for its reactivity with transition
31 metals, particularly at elevated temperatures in the presence of oxygen [28]. Under these conditions it has
32 been shown that carbon atoms will diffuse through into the metal to form transition metal carbides [29]. The
33 criteria needed for these reactions to occur are probably met during diamond polishing at frictional hot spots.
34

35
36 As has been mentioned previously, Couto *et al.* suspected an iron component to polishing debris, supporting
37 at least to some small extent the possibility of chemistry on the scaife surface. Despite this, the scaife
38 preparation process itself has never been investigated. Trying to polish a diamond on a loaded but unprepared
39 scaife leads to large scratches on the surface of the workpiece (Hird: unpublished data). It is thus clear that
40 during the preparation process the scaife undergoes a change leading to conditions favourable to polishing.
41

42 43 **4. Raman spectroscopy of carbon allotropes**

44
45 Raman spectroscopy lends itself particularly well to distinguishing between the many forms of carbon and is
46 thus ideal for use in investigating diamond polishing, where the wear products have already been shown to be
47 mainly sp^2 -bonded. In addition, it is also capable of distinguishing between the many oxides and carbides of
48 iron, which are of particular interest in this research [30]. The application of Raman spectroscopy to the
49 characterisation of carbon allotropes has been reviewed extensively by Knight & White [31], Zaitsev [32] and
50 very recently in a dedicated edition of *Philosophical Transactions* in which the papers by Ferrari & Robertson
51 [33] and Prawer & Nemanich [34] are the most relevant to the present work. As such, only an overview of
52 the signatures one obtains from sp^3 - and sp^2 -bonded carbon materials are outlined here.
53
54
55
56
57
58
59
60

1
2
3 The Raman spectrum of natural diamond is dominated by a very sharp band at 1332 cm^{-1} , and a very weak
4 photoluminescence background. The main Raman band has a FWHM (full width half maximum) of 1.2 cm^{-1}
5 [34] but it may broaden and shift considerably when the material is stressed [32].

6 Visible excitation Raman spectra of sp^2 -bonded carbon material typically have two first-order Raman features
7 – broad bands appearing at around 1357 cm^{-1} and 1580 cm^{-1} . These are usually designated as the D and G
8 bands respectively. The relative intensity of these bands, their exact Raman shifts, and their widths are
9 dependent on the underlying structure of the material. It is possible to distinguish between various amorphous
10 carbons such as charcoal, coke, diamond-like carbon (DLC) and glassy carbons in this way (see [31]). In
11 contrast, graphitic materials containing a greater degree of lattice order than these amorphous materials will
12 lack a strong D band, will show a relatively sharp G band at 1580 cm^{-1} , and a second-order Raman band
13 centred between 2710 cm^{-1} and 2730 cm^{-1} . Polycrystalline graphite also exhibits a disorder band at 1357 cm^{-1} .
14 The Raman signatures of carbon-based oils consist of numerous sharp bands due to the varied functional
15 groups and more complicated structure involved and are readily distinguishable from the various forms of
16 amorphous carbon.
17

18 Another polymorph of diamond is lonsdaleite or hexagonal diamond, and it is said to exhibit a sharp Raman
19 peak appearing between 1315 cm^{-1} and 1326 cm^{-1} [31]. Such features are reported to have been observed on
20 cut (polished) diamond surfaces, on diamond surfaces prepared using thermochemical polishing with hot
21 transition metals [32], and around indentations made on diamond surfaces [35]. A similar feature has been
22 observed in meteoritic carbon. It would appear that none of these claims have been substantiated by X-ray
23 diffraction experiments performed on the same material.
24
25
26
27
28

29 **5. Aim of current research**

30 From the extensive review of the diamond polishing literature summarised here, it is clear that Raman
31 spectroscopy would be beneficial in identifying the wear products produced in both diamond polishing and
32 during scaife preparation. We have chosen to analyse this debris in addition to making a study of as-polished
33 diamond surfaces; *viz.* diamond surfaces which have been polished but are left un-cleaned. These surfaces
34 provide important signs as to how material is removed during the polishing process.
35
36
37
38

39 **6. Experimental details**

40 inVia™ Raman microscopes from Renishaw plc were used in this study. $50\times$ and $100\times$ objective lenses were
41 employed giving a minimum sample volume, in air, of around $1\times 1\times 2\text{ }\mu\text{m}^3$; the collection volume is increased
42 in diamond to varying degrees due to refraction effects at the diamond surface (diamond has a refractive index
43 of *ca.* 2.4) which depends on the focus depth within the sample. Raman spectroscopy represents a significant
44 advantage over other analytical techniques because direct information about chemical structure can be
45 obtained *in situ* with little or no sample preparation and without need of a high vacuum chamber. A wide
46 variety of excitation wavelengths from the near-IR to the UV were provided by lasers operating at 785 nm,
47 633 nm, 514 nm, 442 nm, 325 nm and 244 nm. Of these, the 633 nm excitation (from a HeNe laser) generally
48 proved to offer the best compromise of signal levels and the reduction of fluorescence.
49
50
51
52

53 Debris samples from the preparation process were produced in the laboratory using the standard industrial
54 technique. The scaife plates were manufactured by Coborn Engineering Ltd. and were operated at a rotational
55 speed of 3000 rpm. They were prepared in the traditional fashion by first cleaning the surface with
56 methylated spirits and then applying a very thin film of oil. The oil was either the traditional olive oil or
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
silicone oil (tetramethyltetra-phenyltrisiloxane oil for diffusion pump applications) chosen for its vastly different properties and composition to olive oil. This type of silicone oil is not normally used for diamond polishing. Next, *ca.* 0.2 g to 0.4 g (1 carat to 2 carat) of synthetic diamond grit with a size distribution less than 20 μm was rubbed evenly into the surface. This coating was then 'worked in' using a pellet of sintered diamond (Element 6 product: SYNDAX3) until the initially matt grey layer transformed to a shiny black colour for the olive oil based scaife.

This is one indication used by lapidaries that a scaife is ready for use. However, for the scaife prepared using silicone oil, this state was never attained. Rather, the surface of the scaife became dry and covered with a fine black powder.

14
15
16
17
18
19
20
21
22
23
24
25
26
During this working-in phase, debris samples were collected at time intervals of 1, 5 and 10 minutes. This was in addition to material taken from the scaife before and after polishing, and material ejected from the polishing process itself.

Single-crystalline diamonds synthesized by the high-temperature, high-pressure (HTHP) process were then polished on this newly-prepared scaife. The polished surfaces (area *ca.* 4x4 mm^2) were left un-cleaned for analysis, but appeared mirror-like to the unaided eye and free from surface detritus when viewed under an optical microscope. Polishing was carried out on cube {100} planes in $\langle 100 \rangle$ directions. These polishing directions are known to be 'soft' or easy direction of wear. Crystal orientation was determined by X-ray backscattering (Laue photograph) and was accurate to *ca.* 30 s of arc.

27
28
29
30
31
32
33
34
35
36
37
38
39
40
Reference samples of thermally degraded olive oil and silicone oil were generated by placing small drops of oil on clean glass microscope slides which were then heated to 600 K on a hotplate, so that their burnt products could be analysed.

SYNDAX3 was also studied using Raman spectroscopy as it is an integral part of the polishing process, and takes the place of the more traditional use of boart (a poor quality diamond). SYNDAX3 is a sintered diamond product with silicon and aluminium used as a binder. Another material that may be present on the scaife or in the debris is the plaster of paris and glue mix which is used here to hold the diamond in the dop (the diamond mount) during polishing. This was also examined. As will be seen in the results section, no evidence of either of these materials was found in debris on the scaife, or ejected during preparation.

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

7. Results

Figure 1 shows the Raman spectrum of the olive oil used for preparing the first scaife contrasted with the material obtained when the oil was thermally degraded on a hotplate. The degraded material's spectrum consists of two broad peaks centred around 1360 cm^{-1} and 1580 cm^{-1} , typical of an amorphous carbon like material [31] and lacks the strong C-H bond signatures between 2800 and 3000 cm^{-1} . Olive oil exhibits this type of bonding in addition to C-C bands giving lesser peaks at *ca.* 1300 cm^{-1} , 1400 cm^{-1} and 1650 cm^{-1} .

[Insert figure 1 approximately here]

Silicone oil was found to evaporate with no detectable trace when heated to 700 K. The Raman signature of the unheated oil is easily distinguishable from olive oil, consisting of two sharp bands at *ca.* 1000 cm^{-1} and 1590 cm^{-1} (figure 2).

1
2
3 [Insert figure 2 approximately here]
4

5
6 The spectra from the debris ejected from both the olive oil and the silicone oil scaifes during the first minute
7 of polishing show traces of oil and diamond (figures 3 & 4) in addition to the emergence of a band at 1580
8 cm^{-1} , which is here attributed to the formation of amorphous carbon material.
9

10 [Insert figure 3 approximately here]
11

12 [Insert figure 4 approximately here]
13

14
15 As preparation continues, traces of oil disappear (figures 5 and 7) and the amorphous carbon band becomes
16 stronger. Weak features below 300 cm^{-1} also appear in both the olive and silicone oil scaife debris. These are
17 attributed to iron oxides and when higher laser powers are used, the signal becomes more dominant (figure 5).
18

19
20 [Insert figure 5 approximately here]
21

22 Analysis of debris from polishing using olive oil (figure 6) shows a strong hematite ($\alpha\text{-Fe}_2\text{O}_3$) signature
23 similar to that found in the preparation debris when examined at high laser power ($>15\text{ mW}$), in addition to
24 the D and G amorphous carbon bands.
25

26
27 [Insert figure 6 approximately here]
28

29 The silicone oil scaife debris had particularly broad amorphous carbon bands between 1200 cm^{-1} and 1700
30 cm^{-1} and sometimes exhibited a sharp feature at 1326 cm^{-1} (figure 7).
31

32
33 [Insert figure 7 approximately here]
34

35 A large number of laser excitations (ranging from 244 nm in the ultraviolet to 785 nm in the near-infrared)
36 were used to examine the as-polished diamond surfaces. No evidence could be found of amorphous or
37 graphitic films on the diamond surfaces. This means they are either not present or that they are thinner than 1
38 nm.
39

40 41 **8. Discussion**

42 43 44 **8.1 Diamond debris**

45
46 A clear evolution of chemical species present was found in the debris as scaife preparation proceeds when
47 either silicone- and carbon-based oils were used. In the initial stages of preparation, oil (both silicone and
48 olive oil), diamond and small amounts of amorphous carbon are found in the debris. As preparation
49 progresses, the amount of amorphous carbon increases and the Raman signature of both oils disappears. This
50 may be understood in terms of the thermal properties of the oils. Olive oil burns to produce amorphous
51 carbon, while our investigations have shown that the silicone oil used here evaporates when heated on a
52 hotplate leaving no trace detectable with Raman. Amorphous carbon in the debris from the scaife prepared
53 with silicone oil must therefore be accounted for. The answer lies in the conversion of both the diamond grits
54 on the scaife, and the diamond components of the SYNDAX3 to amorphous carbon. This is another
55
56
57
58
59
60

1
2
3 indication of the reciprocal polishing action between the grits on the scaife and the workpiece [3, 27]. The
4 silicone oil prepared scaife performed very poorly during use tending to score the diamond workpiece badly.
5 It is appropriate here to mention the differences of appearance and touch of the two differently prepared scaife
6 plates. Scaifes prepared with olive oil are generally of a shiny black colour and are slightly sticky to the
7 touch, whereas the scaife surface prepared using silicone oil is covered with a layer of unconstrained fine
8 black powder. It was seen later that this black powder contained significant quantities of diamond particles.
9 Debris from the olive oil prepared scaife contained very few or no diamond particles. The silicone oil
10 prepared scaife shows a distinct diamond Raman band along with the D and G bands of amorphous carbon.
11 Interestingly, the silicone preparation debris sometimes shows another band centred around 1326 cm^{-1} . It is
12 unlikely that this is the 1332 cm^{-1} diamond band with a stress-induced shift as this would indicate too high a
13 tensile stress for the lattice to support. Instead, this feature has variously been attributed to lonsdaleite (the
14 hexagonal sp^3 allotrope of carbon) or stacking faults along $\{111\}$ planes [31, 32, 36]. On the scaife dressed
15 with silicone oil, the grits are not constrained within a sticky carbon layer and are free to move during
16 preparation. It is possible that the resultant tumbling action can cause conditions that are capable of
17 transforming diamond to its hexagonal form.
18
19
20
21

22 Other significant species present in the debris are iron oxides. These originate from the cast iron from which
23 traditional scaifes are manufactured. It was found that the intensity of the iron oxide Raman bands found in
24 the debris is greatly dependent on the power of the laser excitation. Using high laser powers (defined here as
25 *ca.* >10 to 15 mW at the sample), the iron compounds contained within the debris are irreversibly changed
26 from magnetite (Fe_3O_4) (observed at low powers) to hematite ($\alpha\text{-Fe}_2\text{O}_3$). This finding is in agreement with de
27 Faria *et al.* [37] and Bersani *et al.* [29]. As reported by de Faria, this transformation may also be induced
28 during heating the compound with a flame. It is thought that the presence of the hematite in the diamond
29 polishing debris observed with low laser power is due to the intense frictional heating during the polishing
30 process.
31

32 It is unclear from this study whether these iron species influence the polishing mechanism, but in the presence
33 of high temperatures and oxygen, iron behaves as a catalyst, lowering the temperature needed for the
34 formation of sp^2 bonded carbons from diamond [38]. Zaitsev [32] also report the existence of low-energy
35 non-diamond Raman features ($< 700\text{ cm}^{-1}$) on diamond surfaces thermo-chemically treated with hot low-
36 carbon steels. These intensity of the features were also reported to increase with increased exposure to laser
37 power. It is suggested here that these are due to iron oxides rather than carbonaceous phases as Zaitsev has
38 stated.
39
40
41

42 Broad Raman bands in both goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) spectra occur at around 1315 cm^{-1} .
43 Existing literature [32] suggests that bands centred on 1313 cm^{-1} with a width (FWHM) of 30 cm^{-1} to 40 cm^{-1}
44 are observed in meteoric carbon, on diamond surfaces after 'cutting', and after thermo-chemical treatments by
45 hot transitional metals at temperatures above 773 K . Knight and White [31] also suggest that a 1315 cm^{-1}
46 peak is observed in shock synthesised diamond. Under all of these conditions, iron is normally present. It is
47 thus tentatively suggested that peaks around these regions found by other authors are, in fact due to iron
48 impurities being converted into various iron oxides. X-ray analysis using a micro-powder diffractometer
49 carried out on our (olive oil) debris samples reveal the presence of goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$)
50 rather than lonsdaleite, which corroborates this suggestions.
51
52
53
54
55
56
57
58
59
60

8.2 Diamond surfaces

The Raman scattering cross-section for graphite is around 50 times greater than that for diamond for visible excitation wavelengths. Experiments have demonstrated that thin amorphous carbon layers *ca.* 0.1 nm on DLC may be detected using Raman spectroscopy (Hayward: private communication). Detection of such films on diamond, however, is problematic due to the large first order Raman band which tends to mask smaller features. However, even with this peak subtracted, no amorphous or graphitic material, nor olive oil could be detected on as-polished diamond surfaces. This is somewhat peculiar given diamond's oleophilic nature, and the amount of amorphous carbon material present on the scaife formed both during preparation and added to during polishing. If polishing does indeed proceed by a mechanically induced phase transformation [19, 27] and wear rates are *ca.* $40 \mu\text{m min}^{-1}$, the lack of a detectable film could be explained by a planing action of the scaife. Grit particles on the scaife are known to orient themselves during preparation to present a chisel-like edge to the diamond workpiece [3]. Additionally, during an examination of debris from 'soft' direction polishing using a scanning transmission electron microscope (STEM), graphitic clusters in the debris were sometimes found [19]. Van Bouwelen *et al.* argue that the low levels of oxygen found in the debris rule out the possibility of a chemically-aided transformation. If this is correct, then it would appear that the presence of iron in the polishing debris is entirely coincidental.

9. Summary and conclusions

A thorough examination of the debris produced from the preparation of two diamond polishing scaifes indicates that a variety of chemical phase changes occur. The starting materials for preparing a cast-iron scaife are diamond grit and an oil. Traditionally this has been olive oil. It has been found that the oil undergoes a change to amorphous carbon during the preparation process due to the high temperatures developed between the workpiece (SYNDAX3) and the scaife surface. This aids the process of containing diamond grits in the scaife and prevents them from being ejected. The presence of amorphous carbon in the ejected material is also due to reciprocal polishing of the workpiece and the scaife, and later during polishing of diamond. A plausible route by which this conversion may happen is via a mechanical transformation of the diamond by the large shear forces at the diamond-scaife interface as proposed by van Bouwelen *et al.* [19, 27]. However, the presence of iron in all debris perhaps indicates that the process may not be as simple as this and could involve a chemical wear component. All models of polishing should explain this in addition to the absence of a graphitic carbon layer on as-polished surfaces (detectable by Raman).

Based on all evidence collected so far it would appear that by far the most plausible explanation of the mechanism responsible for diamond polishing is via micro-planing, made possible by the large shear stresses at the interface. A thermal mechanism can only conceivably be ruled out, however, by the measurement of the interfacial temperature between a diamond and the scaife. This represents a significant experimental challenge and is currently being investigated.

Acknowledgements

We would like to thank Mr P. Tampkins of Renishaw plc for experimental help. We are grateful to Dr G. Cressey of the Natural History Museum, London for performing the micro-powder diffractometry and to Prof J. E. Field for his continued interest in this area of research and for his comments on the manuscript.

References

- [1] M. Tolkowsky, Research on the abrading, grinding or polishing of diamond. DSc thesis, City and Guilds College, University of London (1920).
- [2] M. F. Ashby & S. C. Lim, *Scripta Metallurgica et Materialia*, **24**, (1990) 805–810.
- [3] J. R. Hird & J. E. Field, *Proc. R. Soc. Lond. A*, **460**, (2004) 3547–3568
- [4] J. R. Hird & J. E. Field, *Wear*, **258**, (2005) 18–25.
- [5] M. Seal, *Proc. Roy. Soc. Lond. A* **248**, (1958) 379–393.
- [6] F. P. Bowden & A. E. Hanwell, *Proc. R. Soc. Lond. A*, **295**, (1966) 233–243.
- [7] M. Casey & J. Wilks, *J. Phys. D: Appl. Phys.*, **6**, (1976) 1772–1781.
- [8] Y. Enomoto & D. Tabor, *Proc. R. Soc. Lond. A*, **373**, (1981) 405–417.
- [9] I. P. Hayward, The friction and strength properties of diamond. PhD thesis, University of Cambridge (1987).
- [10] B. Samuels & J. Wilks, *J. Mat. Sci.*, **23**, (1988) 2846–2864.
- [11] Z. Feng & J. E. Field, *J. Phys. D: Appl. Phys.*, **25**, (1992) A33–37.
- [12] F. M. van Bouwelen, A. L. Bleloch, J. E. Field & L. M. Brown, *Diamond Related Mater.*, **5**, (1996) 654–657.
- [13] S. E. Grillo, J. E. Field. & F. M. van Bouwelen, *J. Phys. D: Appl. Phys.*, **33**, (2000) 985–990.
- [14] A. I. Bailey & M. Seal, *Indust. Diamond Rev.*, **16**, (1956) 145–148.
- [15] A. G. Thornton & J. Wilks, *J. Phys. D: Appl. Phys.*, **9**, (1976) 27–35.
- [16] Z. L. Wang, Z. Feng. & J. E. Field, *Phil. Mag. A*, **63**, (1991) 1275–1289.
- [17] J. R. Hird, The polishing of diamond. PhD thesis, University of Cambridge (2002).
- [18] M. Seal, in *Science and Technology of Industrial Diamonds*, edited by J. Burls (Industrial Diamond Bureau, London, 1967), vol. 1, pp. 145–149.
- [19] F. M. van Bouwelen, J. E. Field & L. M. Brown, *Phil. Mag.*, **83**, (2003) 839–856.
- [20] S. E. Grillo & J. E. Field, *J. Phys. D: Appl. Phys.*, **30**, (1997) 202–209.

- 1
2
3 [21] M. S. Couto, W. J. P van Enckevort & M. Seal, *Phil. Mag. B*, **69**, (1994) 621–641.
4
5 [22] E. M. Wilks & J. Wilks, *Phil. Mag.* **4**, (1959) 158–170.
6
7 [23] C. Phaal, *Phil. Mag.*, **10**, (1964) 887–891.
8
9 [24] T. Evans, & R. K. Wild, *Phil. Mag.*, **12**, (1965) 479–489.
10
11 [25] E. M. Wilks & J. Wilks, *Properties and Applications of Diamond* (Butterworth, Oxford, 1991), pp. 214–
12 227.
13
14 [26] D. Tabor & J. E. Field, in *The Properties of Natural and Synthetic Diamond*, edited by J. E. Field
15 (Academic, London, 1992), pp. 547–541.
16
17 [27] F. M. van Bouwelen, *Phys. Stat. Sol. (a)* **172**, (1999) 91–96.
18
19 [28] S. Evans, in *The Properties of Natural and Synthetic Diamond*, edited by J. E. Field (Academic, London,
20 1992), pp. 181–214.
21
22 [29] M. Yoshikawa, *Proc. SPIE* **1325**, (1990) 210–221.
23
24 [30] D. Bersani, P. P Lottici & A. Montenero, *J. Raman Spectrosc.*, **30**, (1999) 355–360.
25
26 [31] D. S. Knight & W. B. White, *J. Mater. Res.*, **4** (2), (1989) 385–393.
27
28 [32] A. M. Zaitsev, *Optical Properties of Diamond; A Data Handbook*, (Springer, 2001), pp. 69–124.
29
30 [33] A. C. Ferrari & J. Robertson, *Phil. Trans. R. Soc. Lond. A.*, **362**, (2004) 2477–2512.
31
32 [34] S. Praver & R. J. Nemanich, *Phil. Trans. R. Soc. Lond. A.*, **362**, (2004) 2537–2565.
33
34 [35] Y. G. Gogotsi, A. Kailer & K. G. Nickel, *J. Appl. Phys.*, **84**, (1998) 1299–1304.
35
36 [36] S. Bhargava, H. D. Bist, S. Sahli, M. Aslam & H. B. Tripathi, *Appl. Phys. Lett.*, **67**, (1995) 1706–1708.
37
38 [37] D. L. A. de Faria, S. Venâncio Silva & M. T. de Oliveira, *J. Raman spectroscopy*, **28**, (1997) 873–878.
39
40 [38] T. Evans, in *The Properties of Diamond*, edited by J. E. Field (Academic, London, 1979), pp. 403–424.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure captions

Fig.1 Raman spectra of olive oil, and the product formed when the same oil is thermally degraded. This is clearly amorphous carbon.

Fig. 2 Raman spectrum of the silicone oil (Dow Corning 704) used to prepare the second scaife. The oil evaporated with no detectable trace when heated.

Fig. 3 A comparison between the Raman spectrum of the debris produced during the first few minutes of polishing (upper) trace and olive oil (lower) trace. Olive oil is clearly present in the debris (*c.f.* Fig. 1).

Fig. 4 Raman spectra of debris from the first few minutes of the preparation process with silicone oil (upper trace) showed small traces of silicone oil (lower trace).

Fig. 5 The effect of laser power on debris formed during the later stages of the preparation process using olive oil (middle and upper traces). The lower trace is a reference spectrum of hematite ($\alpha\text{-Fe}_2\text{O}_3$). The similarity between this and the debris is striking. Note that any trace of olive oil have now disappeared.

Fig. 6 Raman signature of diamond polishing debris obtained at low laser power. Strong hematite ($\alpha\text{-Fe}_2\text{O}_3$) bands are observed, giving a spectrum similar to that shown in figure 5 after high power laser irradiation. The scaife used was one prepared with olive oil.

Fig. 7 Iron was also found in the debris formed in the latter stages of scaife preparation using silicone oil (see expanded plot showing peaks between 200 cm^{-1} & 300 cm^{-1}). The peak seen at 1326 cm^{-1} is of particular interest since it could suggest lonsdaleite (hexagonal diamond) is present. No trace of silicone oil was found in these samples.

Olive oil (burnt)

Olive oil

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

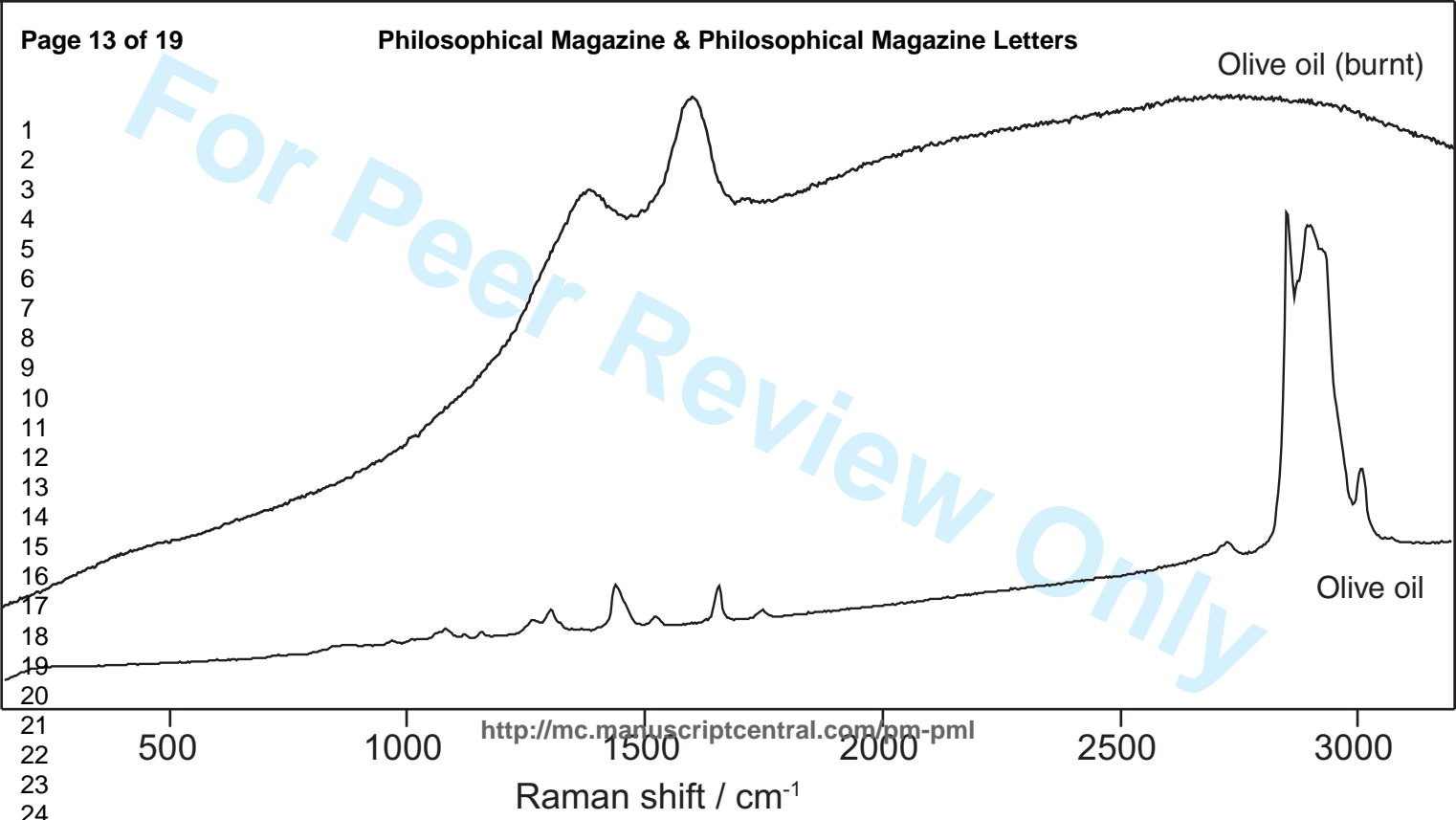
<http://mc.manuscriptcentral.com/pm-pml>

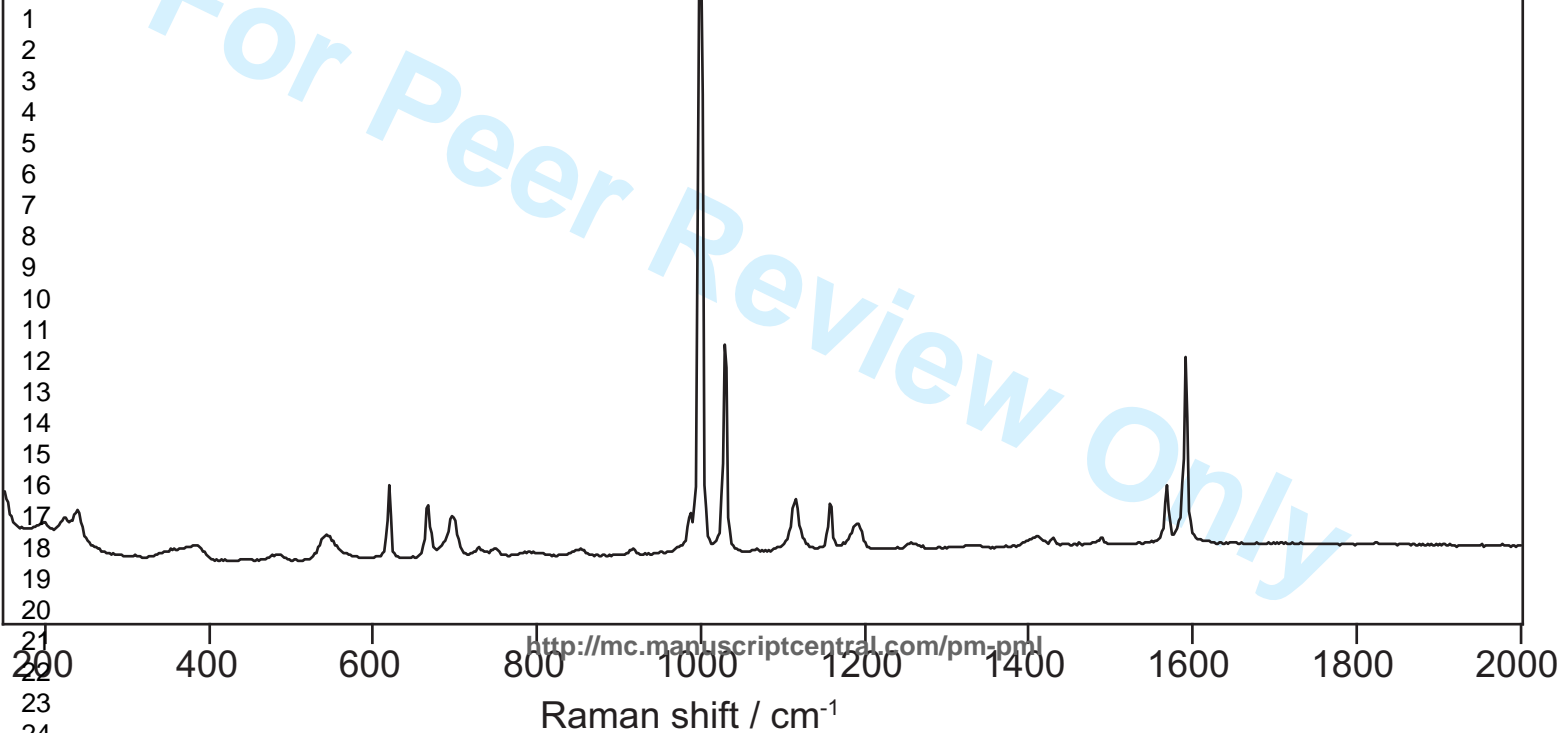
500 1000 1500 2000 2500 3000

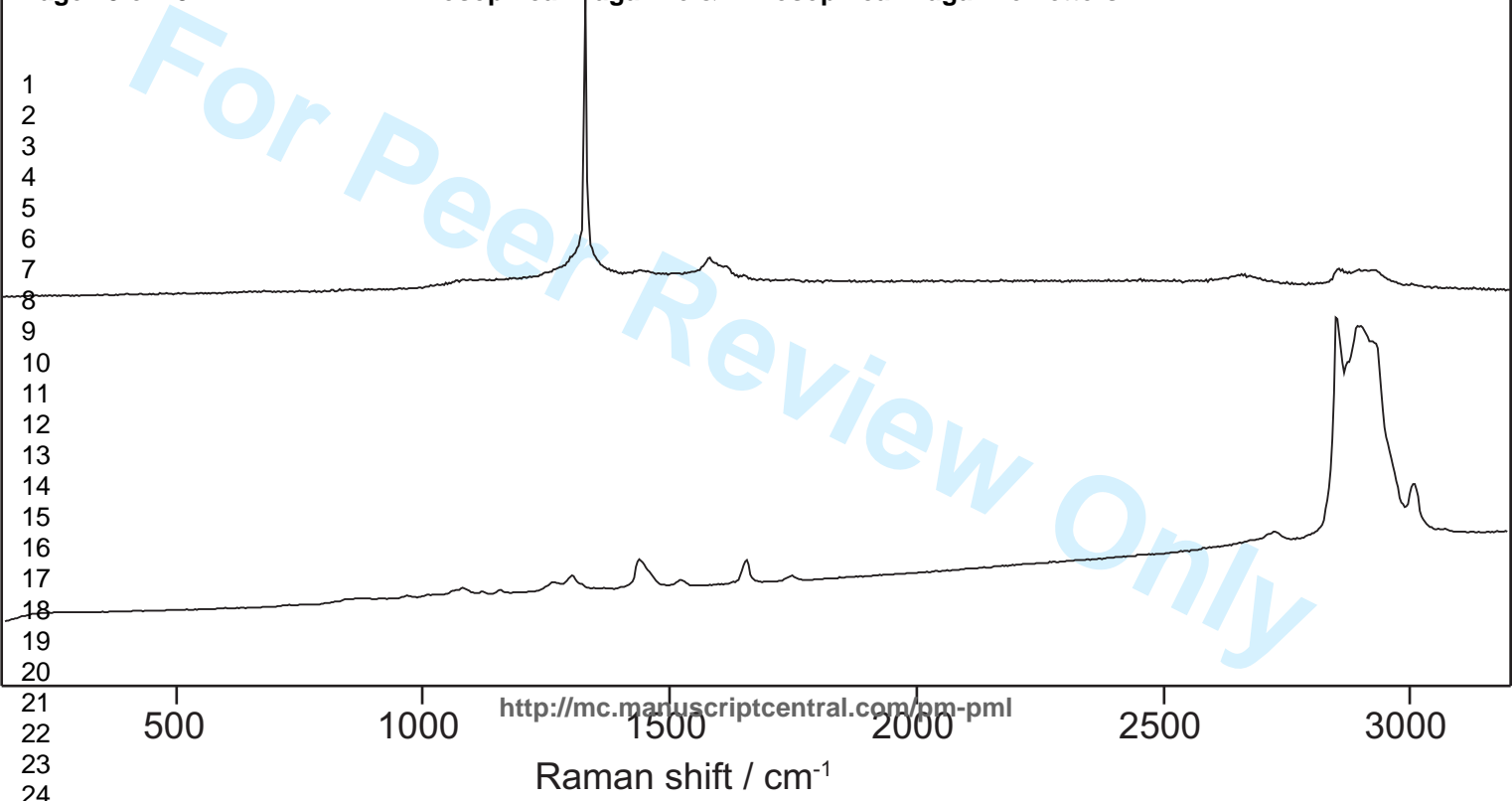
Raman shift / cm^{-1}

21
22
23
24

For Peer Review Only







1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
2021
22
23
24

500

1000

<http://mc.manuscriptcentral.com/pm-pml>

1500

2000

2500

3000

Raman shift / cm^{-1} 