1 **Revision 2**

2 **On the use of unpolarized infrared spectroscopy for quantitative analysis of absorbing**

3 **species in birefringent crystals**

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9 ABSTRACT

10 There is an understandable desire to use simple unpolarized infrared analysis of unoriented

11 anisotropic samples to extract quantitative information, rather than using more demanding

12 polarized techniques. Owing to the fact that unpolarized infrared absorbance in birefringent

13 media deviates from the Beer-Lambert law, previous studies have either warned against using

14 unpolarized spectroscopy for quantitative purposes, or have used flawed error analysis to justify

15 using simple averages of integrated absorbance of multiple absorbance bands as a proxy for total

16 integrated polarized absorbance in the principal spectra. It is shown here that unpolarized

17 infrared absorbance is correctly calculated by averaging in the transmission domain. The errors

18 in estimates of principal absorbance by averaging of unpolarized absorbance spectra are

19 evaluated using correct theory of unpolarized infrared transmission. Correction schemes for

20 integrated absorbance based on linear-absorbance error calculations are shown to be

21 inappropriate. A theory is developed that allows the sum of the polarized principal absorbance

22 spectra to be estimated from multiple unpolarized measurements of randomly oriented samples.

23 The systematic errors that arise when averaging in the absorbance domain are avoided by use of

24   exact theory rather than an approximation. Numerical simulation shows that applying the new

25   procedure to 10 unpolarized measurements of OH stretching bands in olivine results in

26   convergence of the estimated total integrated principal polarized absorbance to within 10% of the

27   true value for a sample size of 10 measurements, but the technique is limited to spectral regions

28   that do not contain absorption bands that are simultaneously intensely absorbing and strongly

29   anisotropic.

30   Keywords: Infrared spectroscopy, unpolarized, quantitative, hydroxyl, olivine

31   INTRODUCTION

32   Infrared (IR) spectroscopy performed in the most commonly used transmission geometry

33   enables the quantitative analysis of absorbing species by application of the Beer-Lambert law. A

34   common application in the Earth sciences is the measurement of hydroxyl, often at trace

35   concentrations in nominally anhydrous minerals (e.g., Rossman 1996). One drawback to such

36   measurements is that birefringent crystals can have strongly anisotropic absorption, leading to

37   large differences in absorbance as a function of the direction of light propagation through the

38   crystal. In such cases, it has been shown that the Beer-Lambert law applies only when the

39   absorbance is measured as the sum of polarized absorbances with the directions of polarization

40   parallel to each of the principal axes of the absorption indicatrix (e.g., Libowitzky and Rossman

41   1996). Consequently, several authors have emphasized that unpolarized infrared spectroscopy

42   cannot be used to make quantitative measurements in anisotropic materials (e.g., Libowitzky and

43   Rossman 1996; Bell et al. 2003). However, a robust determination of the errors associated with

44   unpolarized analysis would enable the use of unpolarized spectroscopy for quantitative

45   measurement in cases where polarized measurement of oriented samples is impractical.

46   Sambridge et al. (2008) and Kovács et al. (2008) developed a theory where the average

47   unpolarized absorbance is used as a proxy for total polarized absorbance. In calculating the

48   errors associated with the approximation, Sambridge et al. (2008) developed an alternative

49   theory for unpolarized absorbance that differs from that given by Libowitzky and Rossman

50   (1996). Here I will show that the theory originally presented in Libowitzky and Rossman (1996)

51   is, in fact, correct. The errors associated with unpolarized measurements will be calculated for

52   some specific examples.

53   THEORY

54   The intensity of light, I, measured at a distance d after passing through an absorbing medium

55   is described by the relationship

56    $$I = I_0\, e^{-\alpha c d},\tag{1}$$

57   where I_0 is the intensity of light entering the medium, α is the molar absorption coefficient and c

58   is the concentration of the absorbing species. The dimensionless quantities transmittance (T) and

59   absorbance (A_n) are defined as

60    $$T = I/I_0\tag{2}$$

61   and

62    $$A_n = -\ln(T) = \alpha c d.\tag{3}$$

63   By convention, the decadic absorbance, A, is used for many practical applications:

64    $$A = -\log_{10}(T) = \varepsilon c d,\tag{4}$$

65   where ε is the decadic molar absorption coefficient, such that

66     $I = I_0 \, 10^{-\varepsilon c d}$.   (5)

67   The natural absorbance (A_n) and corresponding molar absorption coefficient (α) differ from the

68   base 10 equivalents (*A* and ε, respectively) by a constant factor of ln(10). Since the latter are used

69   in the commercial software provided by the manufacturers of Fourier transform infrared (FTIR)

70   spectrometers and by convention are preferred in many fields of quantitative analysis,

71   absorbance hereafter will refer to base 10 absorbance. The choice of logarithm base has no effect

72   on any of the results presented here.

73   The Beer-Lambert law, which is expressed in Equation 4, states that absorbance is

74   proportional to the product of concentration and sample thickness. It is important to note here

75   that absorbance (the exponent in Eq. 5) cannot be measured directly: the physical measurements

76   made in IR absorption spectroscopy are of the intensities of light, detected either after

77   transmission through the sample (*I*), or without a sample in place as a measurement of the

78   'background' intensity (I_0). The FTIR spectrometer allows the analyst to measure the intensity of

79   light as a function of frequency, resulting in a spectrum that may be displayed in units of

80   transmittance or absorbance. The measurement, however, is made in the transmission domain.

81   Unpolarized light can be thought of as a mixture of plane waves with linear polarizations

82   whose vibration directions are uniformly distributed in the plane perpendicular to the

83   propagation direction. When an unpolarized beam of intensity I_0 is incident on an absorbing

84   birefringent crystal, light of a given frequency is split into two polarized rays that can in general

85   be considered as orthogonal, linearly polarized waves (e.g., Sambridge et al. 2008). The incident

86   light intensity in each of the wave vibration directions then is equal to $I_0/2$. The intensity of light

87   emerging from the crystal after travelling along either one of these ray paths may be measured by

88   inserting a polarizer into the beam path. Transmittance as a function of polarization direction is

89   given by:

90    $T(\theta) = T_{max}\cos^2\theta + T_{min}\sin^2\theta,$ (6)

91   where T_{max} and T_{min} are the maximum and minimum transmittance values measured as the

92   polarizer is rotated, and θ is the angle between the direction of polarization during the

93   measurement and the polarizer orientation where $T = T_{max}$ (Libowitzky and Rossman 1996;

94   Sambridge et al. 2008). This relationship was derived elegantly by Sambridge et al. (2008) and

95   can be extended to calculate T for any vibration direction as a function of the values of T for

96   vibration directions parallel to the 3 principal axes of the absorption indicatrix (e.g., Asimow et

97   al. 2006; Sambridge et al. 2008).

98   Combining Equations 2 and 6, for any two mutually perpendicular polarization directions $\theta =$

99   ξ and $\theta = \xi+90°$, the total intensity of the recombined light emerging from the crystal will be

100    $I = I_0/2 \times (T_{max}\cos^2\xi + T_{min}\sin^2\xi + T_{max}\cos^2(\xi+90°) + T_{min}\sin^2(\xi+90°)) = I_0/2 \times (T_{max} + T_{min})$ (7)

101   Thus, the intensity of the recombined light emerging from the crystal with no polarizer in place

102   leads to an unpolarized transmittance (T_{unpol}) of

103    $T_{unpol} = (T_{max} + T_{min})/2.$ (8)

104   The value of A calculated from the measured light intensity is therefore:

105    $A_{unpol} = -\log_{10}\left(\frac{T_{max}+T_{min}}{2}\right).$ (9)

106   This theoretical development arrives at a result identical to Libowitzky and Rossman (1996),

107   who stated that T_{unpol} is the average value of transmittance for all vibration directions in the plane

108   of the sample, given by integration of Equation 6:

109    $$T_{unpol} = \frac{1}{2\pi} \int_0^{2\pi} T(\theta)\, d\theta = \frac{(T_{max} + T_{min})}{2}. \tag{10}$$

110   The foregoing theory is in contrast, however, to the suggestion of Sambridge et al. (2008)

111   that A_{unpol} should be calculated by integration of $A(\theta)$, rather than $T(\theta)$. The formulation of

112   Sambridge et al. (2008) has been adopted by Kovács et al. (2008), who claim that Libowitzky

113   and Rossman (1996) are incorrect in their statement of Equation 10. The justification given by

114   Sambridge et al. (2008) for their alternative theory of unpolarized absorption is that

115   "spectroscopic measurements of IR radiation are often carried out using absorbance, A, rather

116   than transmittance, T". As I have shown in the preceding theoretical development, the reverse is

117   true: when a measurement is made with unpolarized light it is the absorbances in the directions

118   of the electric vectors of the two rays that determine the intensity of light transmitted through the

119   crystal, but the unpolarized absorbance spectrum is calculated (via the commercial software

120   provided with the spectrometer) from the measured intensity of transmitted light. In other words,

121   the intensity of light transmitted through the crystal is correctly calculated by addition in the

122   transmission domain.

123   Note that Equations 7 and 8 imply that the sum of light intensities measured sequentially

124   with any two perpendicular polarizer orientations is equal to the intensity measured without the

125   polarizer in place. In contrast, the theory of Sambridge et al. (2008) contravenes this physical

126   expectation. Consider, also, the case of a highly polarizing sample where T_{max} approaches 1 and

127   T_{min} approaches 0 (As $A \rightarrow \infty$, $10^{-A} \rightarrow 0$). Clearly, Equation 8 in this extreme case returns the

128   expected result of T_{unpol}=0.5 and hence $I=I_0/2$, while integration of A implies T_{unpol}=0.25, i.e.,

129     $I=I_0/4$. The analytical solution leading to this result is presented in the Appendix.

130   The principal aim of Sambridge et al. (2008) and the companion paper, Kovács et al. (2008),

131   is to show the conditions under which averages of unpolarized infrared spectra make a good

132   approximation to the total polarized absorbance, and to evaluate the errors associated with that

133   approximation. Adopting an inaccurate expression for calculating A_{unpol} leads to underestimation

134   of errors. In the following section I will demonstrate the correctness of the theory outlined above

135   by comparison with measured spectra from the literature, and then use the correct theory to

136   reevaluate the errors associated with unpolarized infrared spectroscopy. Finally, a new protocol

137   is developed for estimating the sum of principal polarized absorbances from unpolarized spectra.

138   RESULTS

139   **Comparison with measured spectra**

140   When an infrared measurement is made in transmission mode, the absorbance measured

141   using unpolarized infrared light is close to the average of the maximum and minimum values for

142   polarized absorption only when the maximum absorption intensity is sufficiently small (e.g.,

143   Sambridge et al. 2008). The extent of deviation of the unpolarized absorption from the average

144   of maximum and minimum polarized absorbances was calculated by Sambridge et al. (2008)

145   using an inaccurate formulation for unpolarized absorption, as expressed in the appendix of that

146   paper. In order to illustrate that the expressions for unpolarized absorbance given by Libowitzky

147   and Rossman (1996) and in Equations 8 and 9 of this study are consistent with observation, and

148   to show the real deviation of unpolarized absorption from the average polarized absorption, it is

149   necessary to compare polarized and unpolarized measurements. The ideal sample for this

150   purpose would exhibit strongly anisotropic absorbance and high maximum absorbance values,

151   while remaining within the realm of analysis conditions that are applied to real samples. One of

152   the most common applications of FTIR spectroscopy in Earth sciences is the measurement of H

153   in olivine, a mineral that exhibits exactly these properties. Figure 1 compares polarized and

154   unpolarized FTIR measurements in the OH stretching region of an olivine crystal from Kohlstedt

155   et al. (1996). In this case, where the olivine is oriented such that the direction of light

156   propagation is parallel to the crystallographic **b** axis, the maximum and minimum transmittance

157   values at each frequency are always observed with the polarizer oriented parallel to either the **a**

158   or **c** axis. The unpolarized absorbance, according to Libowitzky and Rossman (1996), is then

159   given by:

160     $A_{\text{unpol}} = -\log_{10}\left(\frac{10^{-A_{\mathbf{a}}}+10^{-A_{\mathbf{c}}}}{2}\right),$ (11)

161   where $A_{\mathbf{a}}$ and $A_{\mathbf{c}}$ are the absorbance values for polarization directions parallel to crystallographic

162   **a** and **c** axes, respectively. Note that the absorbance spectra in Figure 1 are normalized by sample

163   thickness. Owing to the fact that unpolarized absorbance does not scale linearly with thickness,

164   the values of $A_{\mathbf{a}}$ and $A_{\mathbf{c}}$ used in the calculation are those recorded from the original 126 μm thick

165   sample (the sample thickness is recorded in the electronic data file provided by David Kohlstedt)

166   and can be read from the right axis of Figure 1. The unpolarized absorbance according to

167   Sambridge et al. (2008) is calculated as

168     $A_{\text{unpol}} = \frac{1}{2\pi}\int_0^{2\pi} A(\theta)\, d\theta,$ (12)

169   where

170     $A(\theta) = -\log_{10}(10^{-A_{\mathbf{a}}}\cos^2\theta + 10^{-A_{\mathbf{c}}}\sin^2\theta),$ (13)

171   and θ is the angle between the **a** axis and the vibration direction. A Gaussian quadrature

172   algorithm was used for the numerical integration of $A(\theta)$.

173   The measured unpolarized spectrum is matched exactly by the unpolarized spectrum

174   calculated from the measured polarized spectra using Equation 11. In contrast, the alternative

175   theory of Sambridge et al. (2008) overestimates the measured spectrum significantly in the

176   region between 3570 and 3620 cm^{-1} where the maximum and minimum absorbances are strongly

177   offset. Note also that for much of the OH stretching region, the unpolarized absorption in this

178   example is indeed close to the average of the polarized values, suggesting that the difference

179   between integrated unpolarized absorbances and average polarized absorbances may be smaller

180   than the difference in the linear absorbances close to the maxima. A similar verification of

181   Equation 11 is demonstrated in Figure 6 of Libowitzky and Rossman (1996), using a calcite

182   section that displays even more intensely anisotropic absorption bands than does the olivine in

183   Figure 1.

184   **Variations with orientation and thickness**

185   The usefulness of unpolarized spectra from randomly oriented anisotropic samples for

186   quantitative analysis is determined principally by two factors: the convergence of the unpolarized

187   absorbance to a single value, which determines the precision, and the deviation of that value

188   from the polarized absorbance, which detracts from the accuracy of the measurement. To address

189   each of these sources of uncertainty, large populations of unpolarized spectra have been

190   calculated from a set of reference polarized spectra.

191   The reference spectra used for most of the following calculations are taken from Withers et

192   al. (2011), and consist of principal polarized spectra covering the OH stretching region from an

193   olivine that was hydrated in a high-pressure hydrothermal experiment, resulting in the

194   incorporation of 0.2 wt.% H_2O as structurally bound OH groups (Withers et al. 2012). Owing to

195   the high concentration of OH, the sample exhibits intense absorption bands (Figure 2). The

196   highest-frequency peaks at 3612, 3598 and 3579 cm^{-1} have strong absorbance in the $\mathbf{E}||\mathbf{a}$

197   spectrum and weak absorbance in the other principal axis spectra. Another sharp peak at 3566

198   cm^{-1} appears prevalently in the $\mathbf{E}||\mathbf{c}$ spectrum, while the broader absorption band centered around

199   3550 cm^{-1} has strongest absorption in the $\mathbf{E}||\mathbf{b}$ spectrum, and shows less anisotropy than the

200   higher-frequency peaks. This pattern of relative absorption intensity in the principal polarized

201   absorbance spectra is typical of olivines from high-pressure hydrothermal experiments (e.g.,

202   Lemaire et al. 2004; Mosenfelder et al. 2006; Smyth et al. 2006; Litasov et al. 2007), but quite

203   distinct from many natural and lower-pressure experimental samples (e.g., Miller et al. 1987; Bai

204   and Kohlstedt 1993; Bell et al. 2003).

205   The principal polarized spectra shown in Figure 2 are normalized to a thickness of 1 cm.

206   Because principal polarized (but not unpolarized) absorbance follows the Beer-Lambert law

207   (Libowitzky and Rossmann 1996), the spectra can be scaled to any thickness (or concentration)

208   of interest. The following describes how unpolarized spectra are then calculated from the

209   principal axis spectra.

210   A spherical coordinate system with azimuthal angle ψ and polar angle φ is defined such that

211   for an olivine crystal the crystallographic $\mathbf{c}$ direction corresponds to $\varphi=0$, and $\mathbf{a}$ and $\mathbf{b}$ directions

212   correspond to $(\psi, \varphi) = (\pi/2, 0)$ and $(\pi/2, \pi/2)$, respectively. Taking the principal polarized

213   absorbances $A_{\mathbf{a}}$, $A_{\mathbf{b}}$ and $A_{\mathbf{c}}$ as inputs, Sambridge et al. (2008) derive an equation that describes

214   A_{unpol} as a function of incident light direction (their Eq. 60). In the derivation of that equation, an

215   approximation is made whereby the functional form that describes the orientational dependence

216   of transmittance is used for absorbance. Because unpolarized absorbance is correctly calculated

217   by integration in the transmission domain, it is valid simply to replace A with T in the Sambridge

218   et al. (2008) equation, leading to an exact description of T_{unpol} as a function of incident light

219   direction. The unpolarized absorbance for incident direction of (ψ, φ) then is given by:

220    $A_{unpol}(\psi, \varphi) = -\log_{10}\left(\frac{1}{2}(T_\mathbf{a}(\cos^2\varphi\,\cos^2\psi + \sin^2\psi) + T_\mathbf{b}(\cos^2\varphi\,\sin^2\psi + \cos^2\psi) + \right.$

221    $\left. T_\mathbf{c}\sin^2\phi)\right)$ (14)

222   Choosing any two orthogonal vibration directions in the plane of the sample and calculating

223   T from the equation that describes the three dimensional transmission indicatrix (e.g., Asimow et

224   al. 2006; Sambridge et al. 2008) and then applying Equations 8 and 9 leads to the same result as

225   Equation 14. The unpolarized spectrum is calculated from the reference spectra by applying

226   Equation 14 at each frequency of the IR spectrum.

227   A pseudo-uniform distribution of 10,242 incident light directions was calculated by recursive

228   icosahedral subdivision with projection onto a spherical surface. For a given scaling of the

229   reference spectra, an unpolarized spectrum was calculated for each of the 10,242 directions of

230   incident light. Each of the unpolarized spectra shown in Figure 2 represents the average of

231   10,242 spectra calculated in this way. With increasing absorbance (i.e., increasing thickness or

232   concentration), absorbance bands that are strongly anisotropic in the principal polarized spectra

233   decrease in intensity in the unpolarized spectrum relative to more isotropic absorption bands.

234   Thus, in Figure 2 the highest peak in the 30 μm spectrum corresponds to the most intense but

235   most strongly anisotropic 3612 cm^{-1} peak in the principal spectra, while at 50 μm the 3612 and

236   3579 cm^{-1} peaks have equal height, and in the 100 μm spectrum the maximum absorbance is

237   found at 3566 cm^{-1}, the position of the absorption band that is strongest in the $\mathbf{E}\|\mathbf{c}$ principal

238   spectrum, but which is convolved with the broader but more isotropic absorption band centered

239 around 3550 cm^{-1}. When multiple absorption bands are convolved, as is usually the case for OH

240 bands in olivine, it is convenient to use integrated absorbance, which will be denoted by $\int A$, as a

241 measure of their combined absorbance. Figure 2 illustrates how it is the general degree of

242 anisotropy over all of the absorption bands in the spectrum that determines how far the integrated

243 absorbance of the unpolarized spectrum deviates from the average integrated principal spectra.

244 Thus, in an unpolarized spectrum that consists principally of absorption bands related to highly

245 anisotropic peaks such as the high-frequency peaks in the reference spectra in this example, the

246 average integrated unpolarized absorbance ($\int A_{unpol,\ av}$) will deviate strongly from the average of

247 the integrated principal polarized absorbances ($\int A_{tot}/3$), while a spectrum that includes a

248 significant component of more isotropic absorbance, like the broader absorbance peaks at lower

249 frequency in the example spectra, will have $\int A_{unpol,\ av}$ closer to $\int A_{tot}/3$.

250   Figure 3 shows histograms of $\int A_{unpol}$ for the three populations of unpolarized spectra

251 corresponding to 30, 50 and 100 μm thicknesses of the olivine represented by the reference

252 spectra in shown in Figure 2. With increasing absorbance in the reference spectra, $\int A_{unpol,\ av}$

253 deviates further from $\int A_{tot}/3$. For this example, at 30 μm thickness the maximum linear

254 absorbance in the unpolarized spectra is in the range of 0.13-0.27 absorbance units, and $\int A_{unpol,\ av}$

255 is within 8% of $\int A_{tot}/3$. In this particular case, even though the analytical conditions are such that

256 the maximum linear polarized absorbance is greater than the limit of 0.3 absorbance units

257 proposed by Kovács et al. (2008), $\int A_{unpol,\ av}$ does in fact provide a reasonable estimate of $\int A_{tot}/3$.

258 As the total absorbance increases, $\int A_{unpol,\ av}$ provides a progressively inaccurate estimate of

259 $\int A_{tot}/3$. The entire population of $\int A_{unpol}$ for unpolarized spectra calculated for 100 μm thick

260 samples is lower than $\int A_{tot}/3$, and $\int A_{unpol,\ av}$ underestimates $\int A_{tot}/3$ by 19%. The maximum linear

261 absorbance in the unpolarized spectra varies between 0.39 and 0.60 absorbance units which,

262   while higher than ideal, is within the range of values of published measurements of strongly H-

263   enriched olivines from high-pressure experiments (e.g., Kohlstedt et al. 1996). Many such

264   olivines, even when prepared with the minimum practicable sample thickness, have sufficiently

265   strong absorbance in the region of OH stretching that $\int A_{unpol,\ av}$ must depart significantly from

266    $\int A_{tot}/3$ (e.g., Mosenfelder et al. 2006; Smyth et al. 2006; Litasov et al. 2007). If unpolarized

267   measurements of strongly absorbing samples could be corrected to allow accurate estimation of

268   total absorbance the ease of measurement would be greatly reduced. The merits of one such

269   method of correction are discussed below.

Corrections based on linear absorbance

271   It has been proposed that the maximum linear absorbance observed in unpolarized spectra

272   may be used to calculate a correction factor to account for the divergence of $\int A_{unpol,\ av}$ from $\int A_{tot}/3$

273   when non-ideal analytical conditions result in high absorbance values in the regions where strong

274   absorption bands occur (Kovács et al. 2010). A measure of linear absorbance, however, contains

275   no information about absorbance bands in other regions of the spectrum that do not extend to the

276   frequency of the linear measurement. As I have demonstrated above, $\int A_{unpol,\ av}$ becomes closer to

277    $\int A_{tot}/3$ when a significant proportion of the spectrum is more isotropic in nature, so basing a

278   correction on a maximum linear absorbance value that is influenced principally by a strongly

279   absorbing and highly anisotropic absorbance band can lead to overestimation of the correction

280   factor. When the correct theory of unpolarized measurement is used for the calculation of linear

281   absorbance, the two-dimensional linear-absorbance error estimates of Kovács et al. (2008) and

282   Kovács et al. (2010) increase by about a factor of 2 (Note that in the plots of linear-absorbance

283   errors calculated using the *A*-integral theory for unpolarized measurement shown in Figures 1

284   and 10 of Kovács et al. 2008, in the electronic supplement to that paper, and also in the

285   Appendix of Sambridge et al. 2008, several of the contours are wrongly labeled). The correction

286   for integrated absorbance, on the other hand, would be significantly overestimated by use of a

287   linear-absorbance error estimate. This is illustrated in Figure 4, wherein the correction factor,

288   defined as the ratio of $\int A_{tot}$ to $3 \times \int A_{unpol,\ av}$, is plotted against the average maximum linear

289   absorption for the entire population of calculated unpolarized spectra with a given thickness. The

290   curve labeled 'experimental' is defined by the reference spectra shown in Figure 2. Note the

291   point of inflection in the curve at maximum linear unpolarized absorbance of 0.24, which

292   corresponds to the point at which the maximum linear unpolarized absorbance switches from

293   3612 cm^{-1} to lower-frequency peaks (see also Fig. 2). The correction factors calculated from the

294   average of calculated unpolarized spectra are valid only for the specific principal polarized

295   spectra that were used to calculate the unpolarized spectra. When the same calculation is

296   performed using the principal polarized spectra of a natural olivine (KLV23 of Bell et al. 2003),

297   the correction factors fall on a different curve to that defined by the experimental sample (Fig. 4).

298   Other samples with different relative populations of OH species would each have their own

299   sample-specific correction scheme. For example, the Pakistani olivine of Kovács et al. (2008),

300   which has very strong absorbance in $\mathbf{E}\|\mathbf{a}$ and $\mathbf{E}\|\mathbf{b}$ spectra relative to the $\mathbf{E}\|\mathbf{c}$ spectrum over much

301   of the range of OH absorbance, would be expected to have a very large correction factor for high

302   absorption intensities. Of course, in a natural olivine with low H concentrations the sample

303   thickness may be reduced to limit the peak absorption intensities. The purpose of the calculation,

304   however, is to illustrate how the correction factor varies as the absorption profiles of the

305   reference spectra change. The different trends in Figure 4 show that, even though the correction

306   factor does appear to change somewhat systematically with the average maximum linear

307   unpolarized absorbance, the relationship varies from one sample to another.

308   While unpolarized olivine spectra with maximum polarized absorbances that do not exceed

309   0.3 absorbance units provide good estimates for $\int A_{\text{tot}}/3$, it is difficult to estimate the maximum

310   polarized absorbance from unpolarized spectra. Indeed, for a very strongly polarized band that

311   has a minimum polarized absorbance of 0 in the plane of the sample, the unpolarized absorption

312   cannot exceed 0.3 absorbance units (Eq. 9), regardless of the maximum value of polarized

313   absorbance, and how correspondingly large a correction factor would be needed. It is

314   consequently difficult to make a general recommendation for an acceptable level of unpolarized

315   absorbance (Fig. 4).

316   The important point is that correction factors based on empirical correlations with a linear

317   absorbance are not transferrable between samples. In the following section a protocol is

318   described that allows the estimation of $\int A_{\text{tot}}$ from multiple unpolarized spectra, without need for

319   empirical correction.

320   **Estimation of $\int A_{\text{tot}}$ from unpolarized measurements**

321   Despite the offset between $\int A_{\text{unpol, av}}$ and $\int A_{\text{tot}}$, it is theoretically possible to estimate $\int A_{\text{tot}}$ from

322   unpolarized measurements provided that one works in the transmission domain. The technique

323   described by Sambridge et al. (2008) for estimating $\int A_{\text{tot}}$ from unpolarized measurements is

324   based on the approximation of describing the absorbance indicatrix with the equation that

325   correctly describes the transmittance indicatrix. By working in the transmission domain, and

326   using the correct theory of unpolarized absorbance (Eq. 8 and 9), it is possible to estimate $\int A_{\text{tot}}$

327   without approximation. The following theoretical development follows that set out in Sambridge

328   et al. (2008) for absorbance, i.e., the equations applied as an approximation in the absorbance

329   domain are in fact applicable without approximation in the transmission domain.

330   As established previously (Eq. 14), unpolarized transmittance, T_{unpol}, is related to the

331   principal polarized transmittances as:

332    $T_{\text{unpol}}(\psi, \varphi) = \frac{1}{2}(T_{\mathbf{a}}(\cos^2 \varphi \, \cos^2 \psi + \sin^2 \psi) + T_{\mathbf{b}}(\cos^2 \varphi \, \sin^2 \psi + \cos^2 \psi) + T_{\mathbf{c}} \sin^2 \phi)$ (15)

333   Following the same reasoning that Sambridge et al. (2008) used to estimate A_{unpol}, the principal

334   polarized transmittances can be related to the maximum, minimum and average unpolarized

335   transmittance ($T_{\text{unpol, max}}$, $T_{\text{unpol, min}}$, and $T_{\text{unpol, av}}$, respectively). By integrating Equation 15 over

336   all angles (ψ,φ) one obtains $T_{\text{unpol,av}} = \frac{1}{3}(T_{\text{max}} + T_{\text{int}} + T_{\text{min}})$, where T_{max}, T_{int} and T_{min} are principal

337   polarized transmittance and $T_{\text{max}} > T_{\text{int}} > T_{\text{min}}$. By differentiation of Equation 15 with respect to ψ

338   and φ the maximum and minimum unpolarized transmittances, $T_{\text{unpol, max}}$, and $T_{\text{unpol, min}}$, are

339   shown to be equal to $\frac{1}{2}(T_{\text{max}} + T_{\text{int}})$ and $\frac{1}{2}(T_{\text{min}} + T_{\text{int}})$, respectively. Thus,

340    $T_{\text{min}} = 3T_{\text{unpol, av}} - 2T_{\text{unpol, max}}$ (16a)

341    $T_{\text{int}} = 2(T_{\text{unpol, min}} + T_{\text{unpol, max}}) - 3T_{\text{unpol, av}}$ (16b)

342    $T_{\text{max}} = 3T_{\text{unpol, av}} - 2T_{\text{unpol, min}}$ (16c)

343   Given a sufficiently large number of unpolarized spectra, the total polarized absorbance can

344   be estimated. Note that simply averaging in the transmission domain does not provide an

345   estimate of $\int A_{\text{tot}}$. The average polarized absorption cannot be derived from $T_{\text{unpol, av}}$, which is

346   unfortunate, since the latter can be estimated relatively precisely. By applying Equations 16a-

347   16c, each of the three principal polarized absorbances can be estimated, though at a given

348   frequency it is not possible to assign those absorbances to particular principal spectra, since the

349   distribution of relative absorbances varies with frequency. The sum of the principal absorbances

350   (A_{tot}) then is given by addition in the absorbance domain, so that an estimate of $\int A_{tot}$ can be

351   obtained in the following way:

352

353   1. Collect multiple unpolarized FTIR spectra from randomly oriented samples with ideally

354   constant, or else near-constant, thickness. Small variations in sample thickness may be

355   corrected in the absorbance domain.

356   2. Determine the average ($T_{unpol,av}$), maximum ($T_{unpol,max}$) and minimum ($T_{unpol,min}$) transmittance

357   at each recorded frequency.

358   3. Create a total absorbance spectrum by calculating absorbance at each frequency as:

$$A_{tot} = -\log_{10}\left(\left(3T_{unpol,av} - 2T_{unpol,max}\right)\left(2T_{unpol,min} + 2T_{unpol,max} - 3T_{unpol,av}\right)\left(3T_{unpol,av}\right.\right.$$

$$\left.\left. - 2T_{unpol,min}\right)\right) \tag{17}$$

359   4. Integrate the total absorbance spectrum to obtain an estimate of $\int A_{tot}$.

360

361   Unfortunately, the errors in estimated $\int A_{tot}$ tend to be much greater than those calculated by

362   Sambridge et al. (2008) for absorbance domain calculations. In fact, when measuring spectra

363   with strongly anisotropic absorbance, it is possible in a small sampling of unpolarized

364   measurements for $2T_{unpol,\ max}$ to exceed $3T_{unpol,\ av}$ in the region of the most intense absorption

365   bands, in which case Equation 17 fails. In these cases adding further measurements may allow

366   the calculation to succeed, but reducing the sample thickness is more likely to improve the

367   estimate of A_{tot}. In general, unpolarized measurements of samples where the maximum principal

368   polarized linear absorbance does not exceed 1 absorbance unit are unlikely to succumb to this

369   limitation. Under such conditions, though, simply averaging the integrated unpolarized

370   absorbance is likely to provide an acceptable estimate for $\int A_{tot}$. Applying Equation 17 removes

371   the bias toward underestimation of areas, but for a realistically low number of measurements it is

372   doubtful that the new theory improves significantly over taking an average of integrated

373   unpolarized absorption.

374   **Convergence of unpolarized measurements**

375   The number of spectra required for convergence of $\int A_{unpol,\,av}$ can be estimated through a

376   numerical simulation (Fig. 5). Random directions of incidence with spherical coordinates $\theta = m\pi$

377   and $\varphi = \cos^{-1}(n)$, where m and n are random variates on [0,2) and [1,-1], respectively, were

378   chosen using the linear congruential generator by L'Ecuyer with added Bayes-Durham shuffle

379   (Press et al. 2007). For each incident direction, an unpolarized spectrum was calculated from the

380   reference spectra shown in Figure 2 after normalization to a thickness that varied randomly

381   between 45 and 55 μm. Thickness was corrected to 50 μm in the absorbance domain, which adds

382   a small source of simulated measurement error owing to deviation from the Beer-Lambert

383   relationship, and normally distributed noise with a standard deviation equivalent to 0.001

384   absorbance units was added in the absorbance domain. Convergence of $\int A_{unpol,\,av}$ is shown in

385   Figure 5a. In this example, $3\times\int A_{unpol,\,av}$ converges to 70.9 cm^{-1}, which underestimates $\int A_{tot}$ by

386   12%, in agreement with the population average calculated in the preceding section (cf. Fig. 2).

387   Using Equation 17 to estimate $\int A_{tot}$, on the other hand, results in convergence to within 0.5% of

388   the expected value of 80.2 cm^{-1} (Fig. 5b). Note, though, that there is a tradeoff between the

389   standard error resulting from Equation 17 and the systematic error of averaging absorption (Fig.

390   5). Thus, with realistic numbers of measurements (n<30), $\int A_{tot}$ estimated by Equation 17 offers

391   only a minor improvement over the average of integrated unpolarized absorbances.

392   **Uncertainties associated with unpolarized measurements**

393   Without knowledge of the principal polarized spectra, it is impossible to know how far a

394   measurement of unpolarized absorbance at any particular frequency deviates from the average

395   principal polarized absorbance. This is nicely illustrated by the unpolarized spectrum shown in

396   Figure 1, where unpolarized absorbance measured in the region around 3600 cm^{-1} deviates

397   strongly from the average of A_a and A_c, while the same measured absorbance values at ~3560

398   cm^{-1} are very close to the average of A_a and A_c. Using multiple measurements to estimate the

399   total principal polarized absorbance by way of Equation 17 can lead to large errors over the

400   frequency ranges where principal absorbance is strongly anisotropic. This is because anisotropic

401   principal absorbance can lead to a long tailed and potentially skewed distribution of T_{unpol}, from

402   which it is difficult to estimate maximum, minimum and average values with a small sampling.

403   Moreover, with no knowledge of the principal polarized spectra and a small sampling of

404   unpolarized measurements, the uncertainty in A_{tot} estimated using Equation 17 cannot be

405   assessed. Thus, using unpolarized measurements to estimate $\int A_{tot}$, either by applying Equation 17

406   or by averaging integrated absorbance, relies on the unknown principal polarized spectra having

407   an acceptable degree of anisotropy. For this reason, incircumspect application of Equation 17 is

408   to be avoided.

409   Partial polarization of unpolarized beams within the spectrometer can provide an additional

410   source of uncertainty that is not considered in the foregoing theoretical calculations. The effects

411   of partial polarization and polarizer efficiency are discussed by Libowitzky and Rossman (1996).

412   CONCLUSIONS

413   1. Unpolarized absorbance is equal to the logarithm of the average of any two perpendicular

414   measurements of transmittance with polarization directions in the plane of the sample, as

415   previously stated by Libowitzky and Rossman (1996). The systematic deviation of linear

416   unpolarized absorbance from the average principal polarized absorbance is consequently

417   underestimated by alternative theories of unpolarized absorbance (Sambridge et al. 2008;

418   Kovács et al. 2008; Kovács et al. 2010).

419   2. There is no theoretical justification for applying a correction based on the deviation of a

420   linear absorbance in one part of the spectrum from the average polarized absorbance at that

421   frequency to the integral of multiple absorbance bands. The correction scheme proposed by

422   Kovács et al. (2010), while based on an underestimation of the correction factor for linear

423   unpolarized absorbance, results in over-correction when applied to integrated unpolarized

424   OH absorption bands in the olivines considered here.

425   3. Based on calculations of unpolarized spectra in the OH-stretching region from natural and

426   hydrothermally annealed olivines, averages of >10 unpolarized spectra where the maximum

427   linear absorbance does not exceed 0.3 absorbance units are expected to give a reasonable

428   estimate of $\int A_{tot}$. This conclusion is valid only for samples where the average degree of

429   anisotropy in the principal polarized spectra is not significantly greater than that of the

430   examples used in the simulations.

431   4. Multiple unpolarized spectra of randomly oriented samples can be used to estimate $\int A_{tot}$ by

432   application of Equation 17. Given a sufficient number of measurements, the new theory

433   reproduces $\int A_{tot}$ without systematic bias, but is limited by sensitivity to the shape of the

434   unpolarized transmittance distribution. For reasonably low numbers of measurements, the

435   new procedure is not a significant improvement over averaging integrated unpolarized

436   absorbance.

437   5. The error of an estimate of $\int A_{tot}$ based on unpolarized measurements varies with the degree of

438   anisotropy of the principal polarized spectra, and cannot be estimated accurately from a small

439   sampling of unpolarized spectra.

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495   FIGURE CAPTIONS

496   **Figure 1**

497   Comparison between measured and calculated unpolarized infrared spectra of olivine in the OH

498   stretching region. Polarized and unpolarized spectra from an olivine that was hydrothermally

499   annealed at 5 GPa and 1100 °C are from Kohlstedt et al. (1996) and were measured in a 126 μm

500   thick section that was oriented such that the direction of light propagation was parallel to the **b**

501   axis. Polarized spectra recorded with the directions of polarization parallel to the **a** and **c** axes are

502   labeled **E**∥**a** and **E**∥**c**, respectively, and the unpolarized spectrum is plotted as a dashed line.

503   Unpolarized spectra were calculated from the **E**∥**a** and **E**∥**c** spectra using the '*A* integral' theory

504   of Sambridge et al. (2008) and the '*T* integral' theory of Libowitzky and Rossman (1996). The

505   average of the **E**∥**a** and **E**∥**c** spectra, corresponding to the '*A*-theory' approximation of Sambridge

506   et al. (2008), is shown for comparison. Absorbance values read from the right axis are for a

507   sample thickness of 126 μm.

508   **Figure 2**

509   Calculation of average unpolarized absorbance spectra for olivine in the OH stretching region.

510   Following the method described in the text, unpolarized spectra were calculated from the

511   principal polarized spectra of an olivine containing 0.2 wt. % H_2O (M475 of Withers et al. 2011),

512   shown in the inset. For each sample thickness labeled on the plot, 10^4 unpolarized spectra were

513   synthesized for evenly distributed directions of light propagation. Averages of calculated spectra

514   are shown.

515   **Figure 3**

516 Histograms of integrated absorbance in the range 3100-3800 cm^{-1} for populations of unpolarized

517 spectra calculated with 10^4 evenly distributed directions of light propagation in an olivine. The

518 polarized absorbance spectra used in the calculation (see Fig. 2) were scaled to the equivalent of

519 30, 50 and 100 μm thicknesses of olivine with 0.2 wt. % H_2O (or equivalent products of

520 thickness and concentration). Unpolarized absorbances were normalized to 1 cm sample

521 thickness for comparison with the average integrated absorbance of the normalized principal

522 polarized spectra, indicated by the vertical dashed line.

523 **Figure 4**

524 Correction factors, defined as the ratio of the average integrated absorbance of principal

525 polarized spectra ($\int A_{tot}/3$) to the average integrated unpolarized absorbance ($\int A_{unpol,\ av}$). Unbroken

526 curves represent averages of large (10^4) populations of calculated spectra with evenly distributed

527 light propagation directions (see text for details). The population-average correction factors are

528 plotted against the average maximum linear absorbance in the unpolarized spectrum. The

529 calculation is unique to a set of principal polarized spectra. Spectra from an experimental sample

530 (M475, shown in Fig. 2) and a natural sample (KLV23 of Bell et al. 2003) are used to create two

531 examples. These correction factors are not transferrable between samples that have different

532 patterns of principal polarized absorption. The correction scheme described by Kovács et al

533 (2010), which is based on the linear-absorbance error estimates of Sambridge et al. (2008)

534 calculated using the 'A integral', is also shown. The grey hatched area falls outside of the space

535 of possible population-average correction factors for a single absorption band with a Gaussian

536 shape.

537 **Figure 5**

538   (a) Convergence of averaged integrated absorbance of unpolarized infrared spectra of olivine

539   ($3 \times \int A_{unpol}$), calculated from the reference spectra shown in Figure 2 after normalization to 50 μm

540   thickness. Unpolarized spectra were calculated using Equation 14 for random directions of light

541   propagation (see text for details). Error bars are standard error of the mean. The total integrated

542   absorbance of the principal polarized spectra ($\int A_{tot}$) is marked by the dashed line. (b)

543   Convergence of estimated $\int A_{tot}$ calculated from unpolarized spectra using Equation 17.

544

545   APPENDIX 1

546   **Calculation of T_{unpol} for a perfect polarizer by integration of absorbance.**

547   According to the alternative theory of unpolarized absorption, unpolarized absorbance is

548   given by:

549    $A_{\text{unpol}} = -\frac{1}{2\pi} \int_0^{2\pi} \log_{10}(10^{-A_{\text{max}}} \sin^2 \theta + 10^{-A_{\text{min}}} \cos^2 \theta) \, d\theta,$ (18)

550   where θ is defined with respect to the direction of minimum absorbance (Sambridge et al. 2008).

551   For a perfect polarizer, $A_{\text{max}} = \infty$ and $A_{\text{min}} = 0$. The term inside the integral then reduces to

552    $\log_{10}(\cos^2 \theta)$:

553    $A_{\text{unpol}} = -\frac{1}{2\pi} \int_0^{2\pi} \log_{10}(\cos^2 \theta) \, d\theta$ (19)

554   The symmetry of the function $\log_{10}(\cos^2(\theta))$ suggests

555    $A_{\text{unpol}} = -\frac{2}{\pi} \int_0^{\pi/2} \log_{10}(\sin^2 \theta) \, d\theta$ (20)

556    $= -\frac{4}{\pi} \int_0^{\pi/2} \log_{10}(\sin \theta) \, d\theta$ (21)

557    $= -\frac{4}{\pi \ln 10} \int_0^{\pi/2} \ln(\sin \theta) \, d\theta.$ (22)

558   The solution to the definite integral in Equation 22 is $-\pi/2 \ln(2)$ (Euler 1769), so:

559    $A_{\text{unpol}} = 2 \log_{10}(2) = -\log_{10}(4^{-1}),$ (23)

560   leading to an incorrect value for the transmittance of a polarizer:

561    $T_{\text{unpol}} = \frac{1}{4}.$ (24)