1 **Revision 1**

2

3 **Quantitative analyses of powdered multi-minerallic carbonate aggregates using a portable**

4 **Raman spectrometer.**

5

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26   **Abstract**

27

28   Mg-Ca carbonates are an important group of industrial minerals which frequently occur

29   intimately intermixed in natural settings and are traditionally assessed for phase purity by X-ray

30   diffraction (XRD). In this study Raman spectroscopy is employed to quantify the modal

31   abundance of hydromagnesite [$Mg_5(CO_3)_4(OH)_2.4H_2O$], huntite [$CaMg_3(CO_3)_4$], dolomite

32   [$MgCaCO_3$] and magnesite [$MgCO_3$], in powdered mixtures constructed from fabricated

33   reference materials. Particle size distributions were assessed by scanning electron microscopy

34   and laser diffraction. Raman analyses performed using a portable instrument were conducted at

35   25°C and at atmospheric pressure. XRD was employed to validate the accuracy and precision of

36   Raman measurements. Monovariable and multivariable methods were employed to provide

37   quaternary quantification from the spectroscopic data. For monovariable calibration the

38   amplitude of the peaks was plotted against the measured weight ratios of the four mineral phases.

39   Overlapping bands were resolved using the Gaussian Lorentzian method. Chemometric methods

40   were used to perform the multivariable calibration. The overall lowest error on component values

41   was obtained by Principal Component Regression with application of Standard Normal Variate

42   correction. The quantifications derived by Raman spectroscopy and XRD show close agreement.

43   Hence, evidence suggests that a reliable four-way calibration program to screen the purity of

44   carbonate assemblages can be constructed, providing particle size effects are constrained and

45   spectroscopic operating conditions are uniform.

Introduction

46

47

48 The carbonate minerals dolomite [$MgCaCO_3$], magnesite [$MgCO_3$] hydromagnesite

49 [$Mg_5(CO_3)_4(OH)_2.4H_2O$] and huntite [$CaMg_3(CO_3)_4$] frequently occur intimately intermixed in

50 recent sediments. The latter two minerals are subject to progressive replacement by the

51 equilibrium assemblage magnesite-dolomite during diagenesis (Kinsman 1967; Lipmann 1973;

52 Stamatakis 1995). Collectively, the four Mg-Ca carbonate minerals are also commercially

53 important, with applications in finely powdered forms, in many branches of industry, e.g.

54 pharmaceutical, cosmetic, paint formulations, flame retardants and bulk applications.

55 Commonly, the purity of the powders with respect to the modal abundance of the different

56 carbonate mineral phases is of prime concern. For instance hydromagnesite and huntite are often

57 used in conjunction in customized mixtures (Hollingberry and Hull 2010). Hence, a method that

58 facilitates rapid and accurate characterization of carbonate mineral assemblages is important.

59

60 Mineral identification and mineral assemblage characterization are commonly conducted by

61 X-ray diffraction (XRD). The technique is almost invariably laboratory based and frequently

62 remote from field exposures and sites of mineral processing. In addition, quantitative

63 determination of assemblages by XRD can be problematic (Vagenas and Kontoyannis 2003) and

64 the degree of long-range crystal order of synthetic and natural Mg-Ca carbonates can be variable

65 (Hopkinson et al. 2008, 2012). Another analytical technique used for quantitative analysis of

66 minerals is infrared spectroscopy (IR), for which the sample particle size requirements are *ca*

67 2µm or less (Vagenas et al. 2003). However, IR spectral bands of the Mg-Ca carbonates are

68 typically relatively broad, often with indefinite baselines, and show significant overlap (White

69   1974).

70

71   Raman spectroscopy is a well established non-destructive analytical technique that offers rapid

72   identification of materials and their polymorphs (Dandeu et al. 2006). Current development of

73   portable Raman spectrometers, ranging in size from handheld to larger transportable equipment,

74   could also bring new possible industrial or geological applications e.g. field identification of

75   minerals, mapping of quarries or on site quality assurance of processed ores. The Raman

76   measurements under field conditions have been tested by e.g. Jehlicka et al. (2011), Vitek et al.

77   (2012) and also few pioneer studies investigated their reliability for a possible quantitative

78   detection with applications aimed at planetary exploration (Culka at al 2011, Vandenabeele et al.

79   2012).

80   The Raman spectroscopic technique is often used as a semi-quantitative method, using line ratios

81   or standard addition, thereby producing generally simple calibrations based on single peak height

82   or area measurements (Vagenas et al. 2003; Noguchi et al. 2009). Amongst the quantitative

83   investigations of carbonate mineral phases by Raman, binary mixtures of calcite in dolomitic

84   marble have been investigated by standard addition (Vagenas and Kontoyannis 2003) and by

85   monovariable calibration by peak height against weight. The same techniques have been applied

86   to calcium carbonate fillers in high-density polyethylene (Pakjamsai and Suwanprateeb 2000)

87   and silicate and calcium carbonate assemblages using Raman micro-spectrometry (Noguchi et al.

88   2009). However, less attention has been paid to quantitative analysis of ternary or multi-

89   component admixtures of carbonate mineral assemblages although multivariable methods,

90   utilizing all Raman active bands i.e. Partial Least Squares (PLS), have been successfully

91   employed to quantify the modal abundances of calcite, aragonite and vaterite in powdered

92   mixtures of the three $CaCO_3$ polymorphs (Dandeu et al. 2006; Jehlicka et al. 2009). Close link

93   between Raman band position shifts and chemical composition of rhombohedral carbonates

94   forming solid solutions in Ca-Mg-Fe system was showed by Rividi et al. (2010). Moreover

95   mixtures of calcium, strontium and barium carbonates have also been investigated by Raman

96   spectroscopy, employing the full width at half maximum (FWHM) intensity of the v_1 modes of

97   the carbonate anion for the three mineral phases (Kaabar et al. 2011). However, at present a

98   standard methodology for quantitative calibration of multi-minerallic carbonate assemblages is

99   absent (Fevotte 2007) and accounts of quaternary calibration procedures for carbonate

100   assemblages are lacking. To this end, this paper explores the Raman spectroscopic signature of

101   powdered mixed assemblages of dolomite, magnesite, huntite and hydromagnesite, based on the

102   intensity of Raman peaks and known weight fractions of admixtures of the four mineral phases.

103

104   **The Raman spectra of magnesium and calcium carbonates**

105

106   The carbonate anion $[CO_3^{2-}]$ forms a planar triangle with molecular symmetry D_3h. In isolation

107   its vibrational spectrum consists of four normal (internal) modes - v_1 symmetric stretch (Raman

108   active), v_2 out-of-plane bend (IR active), v_3 asymmetric stretch and v_4 in-plane bend, which are

109   Raman and IR active. In carbonate minerals the $[CO_3^{2-}]$ anion is bonded to cations within the

110   crystal lattice and operates under symmetrical constraints, distinctive to the specific mineral

111   species (White 1974). The vibrational spectra and band assignments of the Mg-Ca carbonates are

112   well documented (e.g. Edwards et al. 2005; Frost and Dickfos 2007a). The Raman spectra are

113   divisible into three wavenumber regions: 1500–1000, 1000–500, and 500–100cm^{-1} (Edwards et

114   al. 2005; Frost and Dickfos 2007a, 2007b; Scheetz 1977; Frost 2011). In general, bands at

115   wavenumbers above $500cm^{-1}$ are due to the internal motions of the molecular carbonate anion

116   (internal modes). Those below $500cm^{-1}$ are due to motions involving the entire lattice cell (lattice

117   modes). Within the $1500–1000cm^{-1}$ region, the symmetrical stretching mode v_1 of the $[CO_3^{2-}]$

118   anion is the strongest band observed in the Raman spectrum of the four carbonate mineral

119   phases. The Raman shift of the v_1 mode for magnesium carbonates occurs at higher

120   wavenumbers than for calcium bearing counterparts. However, in the case of the double

121   carbonate minerals, the v_1 position depends on whether the Ca and Mg cations are ordered into

122   two different layers as is the case for dolomite, or whether the crystal has a superstructure of

123   calcite with cation ordering within one layer as is the case for huntite (Scheetz 1977). For all Mg-

124   Ca carbonates the v_3 asymmetric stretching mode shows low intensity peaks at ca $1450cm^{-1}$. The

125   v_4 in-plane bending mode occurs as a weak band at ca $700cm^{-1}$ (Edwards et al. 2005). The lattice

126   modes involve translatory and rotational oscillations (Gunasekaran 2006) and can be diagnostic

127   of specific mineral phases. For instance, dolomite and magnesite show high intensity peaks at

128    $300cm^{-1}$ and $330cm^{-1}$ respectively (Edwards et al. 2005).

129

130   **Analytical methods**

131

132   Raman analysis was conducted at the University of Brighton U.K., employing a portable Raman

133   spectrometer (Perkin Elmer, Raman IdentiCheck), fitted with a 785nm laser and with CCD

134   detector air cooled to -50°C. The dimensions of the spectrometer are 585 x 565 x 400mm (35kg)

135   and the measurements were performed using a fibre optic probe with a 100μm spot size at a

136   working distance of 7.5mm. The samples were measured in a spectral range of $1500-150cm^{-1}$ at a

137   resolution of $2cm^{-1}$, the laser power is user adjustable between 100 and 10mW. Each spectrum

138   was collected from 8 scans for 2 seconds using 70mW laser power at room temperature and

139   repeated six times on randomly selected subsamples in order to ensure representative spectral

140   information. The spectra were averaged, baseline corrected and deconvoluted. Data manipulation

141   was performed using the software Spectrum (Perkin Elmer) and PeakFit (Jandel, Scientific

142   Software). The multivariable methodologies based on Principal Component Regression (PCR+)

143   and Partial Least Squares (PLS) were conducted with software Spectrum Quant+ (Perkin Elmer)

144   applied to the spectra. Particle sizes and shapes of the powdered aggregates were monitored by

145   scanning electron microscopy (SEM), model: Zeiss Sigma FEG-SEM and, a Malvern

146   Mastersizer 2000 particle size analyzer (PSA), with a Malvern Hydro 2000G dispersion unit.

147   Both analytical techniques were performed at the University of Brighton U.K.

148

149   X-ray powder diffraction data (performed at the Natural History Museum, London, U.K.) were

150   collected using a Nonius PDS 120 powder difffraction system with an INEL curved position

151   sensitive detector (PSD). This detector has an output array of 4096 digital channels representing

152   an arc of 120°2θ and permits the simultaneous measurement of diffracted X-ray intensities at all

153   angles of 2θ across 120° with a static beam-sample-detector geometry. Copper Kα₁ radiation was

154   selected from the primary beam using a germanium 111 single-crystal monochromator and slit

155   system. Horizontal and vertical slits were used to restrict the beam to 0.10 by 5.0mm

156   respectively. For phase identification, each powdered sample was mounted on a single-crystal

157   sapphire substrate as a thin smear. For phase quantification, each mixture sample was packed

158   into a 1mm deep well. All measurements were made in reflection geometry with the sample

159   surface (spinning in its own plane) at an angle of 5° to the incident beam. Data collection times

160   were 15 minutes for each sample. NIST silicon powder SRM640 and silver behenate were used

161 as external 2θ calibration standards and the 2θ linearization of the detector was performed using

162 a least-squares cubic spline function. Search-match procedures using STOE WinXPOW

163 software, containing the Powder Diffraction File PDF-2 supplied by the International Centre for

164 Diffraction Data (ICDD), were employed to identify the mineral phases present. The mixture

165 phase proportions have been determined by proportional matching the single-phase patterns

166 against each of the mixture patterns using a least-squares fitting program (LinkFit version 1.0.4).

167

168 **Reference material fabrication**

169

170 Mineral reference materials were fabricated from natural samples of huntite, dolomite and

171 magnesite, sourced from the geological collection of the University of Brighton. Synthetic

172 hydromagnesite [$Mg_5(CO_3)_4(OH)_2.5H_2O$] purchased from Fisher Scientific (lot no.1129583) was

173 used as the nearest match to natural hydromagnesite, due to high impurity concentrations in all

174 sampled natural hydromagnesite materials. The dolomite sample contained $CaCO_3$ impurities as

175 evident by staining with 0.25% Alizarin Red S in 0.25% hydrochloric acid (HCl). Based on

176 reaction rates with acids, the dolomite standard was purified by treatment with 0.05M HCl and

177 0.1M HCl until the red staining disappeared and was then washed with deionised water. All

178 minerals were powdered, using a ZrO_2 (Fritsch, planetary monomill) ball mill operating at

179 400rpm for 10min, and sieved through a 100μm mesh to ensure homogeneity.

180

181 XRD analysis of the huntite, hydromagnesite and magnesite reference materials were void of

182 resolvable mineral impurities (Figure 1a), suggesting that if impurities are present they are at

183 concentrations below the detection limit, i.e. less than *ca* 2% modal abundance. Dolomite

184   contained traces of calcite which is detectable at 1-2% level. An assessment of the amount of

185   calcite in the dolomite standard by quantitative phase analysis (QPA) XRD was repeated three

186   times and gave consistent results of 0.024-0.025 fit fraction for calcite, equivalent to 1.6-1.7wt%

187   calcite. The dolomite concentrations in mixtures of the reference materials were recalculated

188   accordingly. The Raman active vibrational modes for the four fabricated reference materials

189   (Figure 1b) are in good agreement with published values (Edwards et al. 2005).

190

191   SEM analysis indicates that the dolomite sample consists of well cleaved tabular crystals, up to

192   *ca* 8μm in length (Figure 2a). The crystals show locally intense conchoidal fracturing and are

193   interspersed with abundant finer grained anhedral particles which range in size from a few

194   microns to <0.5μm. The particles show a presence of Mg, Ca and C, with no Mn or Fe or trace

195   metals detected, suggesting that the dolomite closely approaches stochiometric [$MgCaCO_3$]. The

196   huntite sample consists of uniform platy rhomboidal crystals which range in size from 1.5 to

197   0.5μm, arranged in *ca* 10-20μm wide agglomerates (Figure 2b) which show a correspondence of

198   Ca, Mg, and C. The synthetic hydromagnesite sample consists of agglomerates of well cleaved

199   platy crystals, showing uneven fracture, with particle sizes ranging from *ca* 1.5μm to *ca* 100nm

200   (Figure 2c). The magnesite sample consists of conchoidal fragments of the mineral, which range

201   in size from *ca* 2μm to *ca* 100nm, together with lesser quantities of large (2-6μm length) variably

202   fragmented equant rhombic crystals, which display well developed cleavages (Figure 2d). The

203   powder is devoid of evidence for elements other than Mg and C, suggesting that the crystals

204   approach stochiometric [$MgCO_3$]. PSA analysis of the fabricated reference materials indicates a

205   measured mode grain size of 4-7μm. The minerals show a size distribution profile consistent

206   with SEM evidence for agglomerations of particle aggregates (Figure 3).

207

208   The four reference material powders were weighed and mixed in varying proportions. The

209   sample mixtures (1.5gram) were weighed using 4-place analytical balances and manually mixed

210   for 20 minutes in glass vials (25ml). Mixtures of the minerals were constructed with huntite and

211   hydromagnesite as the main components. Dolomite and magnesite were used in modal

212   abundances up to 16% w/w (Table 1). The homogeneity and particle size distribution of the

213   mixed powders was monitored by SEM (e.g. Figure 2 (e) and (f)). Spectroscopic analyses were

214   performed on the day of mixture preparation from lightly pressed samples in aluminum sample

215   holders. Twenty samples were prepared to construct the quantification models. To provide

216   overall method error, fifteen randomly selected samples were employed in calibration and five

217   mixtures were used to test the quantification procedures.

218

219   **Results**

220

221   **Quaternary quantification of Mg-Ca carbonate mixtures by Raman**

222

223   The spectra of four component carbonate mixtures show variable numbers of lines of different

224   intensities and merged multi-component bands. In particular, the two strong intensity doublet

225   peaks assigned to the C-O symmetric stretch (v_1 mode) overlapping huntite with hydromagnesite

226   and dolomite with magnesite occur in the ranges of ca 1121-1118cm^{-1} and 1097-1095cm^{-1}

227   respectively (Figure 4a). In the lattice mode region the spectra are characterized by a number of

228   medium and low intensity vibrations, which can be assigned to the four constituent minerals. The

229   v_1 modes of the constituent minerals and peaks in the lattice mode region (magnesite at 330cm^{-1},

230   dolomite 300cm^{-1}, huntite 272 and 252cm^{-1} and hydromagnesite 202 and 184cm^{-1}) were used to

231   identify the contribution of each mineral phase to the observed spectra (Figure 4) and employed

232   to construct quantitative calibration procedures, applying monovariable and multivariable

233   regressions to the spectra.

234

235   The monovariable calibration method was created using maximum peak heights of the most

236   intense bands plotted against weight fraction. Huntite and hydromagnesite were quantified using

237   the v_1 mode peaks. In the case of magnesite and dolomite this was done in conjunction with the

238   medium to high intensity lattice mode bands at 330cm^{-1} and 300cm^{-1} respectively. The

239   calibration was described by a linear regression trend line for each mineral (Figure 5), R^2 values

240   and an error on test samples were calculated. The correlation coefficients for individual minerals

241   were R^2 = 0.9860, 0.9859, 0.9734 and 0.9505 for huntite, hydromagnesite, dolomite and

242   magnesite respectively (Figure 5). The average difference between the calculated and real value

243   of test sample mineral concentration (sample error) was on average 20% of its value. To evaluate

244   repeatability of the spectroscopic measurements and data manipulation, replicate measurements

245   were taken on one sample to provide six groups of six measurements. Spectra in each group were

246   averaged, baseline corrected, deconvoluted, peak fitted and compared. The relative standard

247   deviation ranged from 2.1% for a one phase sample to an average relative standard error of 9.6%

248   for quaternary mixtures on v_1 peak height that was used in the monovariable model. This error

249   includes potential effects of mixture inhomogeneities.

250

251   Two multivariable models were created using PCR+ and PLS, with and without an applied

252   normalization algorithm, i.e. Standard Normal Variate (SNV) for both chemometric methods.

253   SNV transformation was used to remove the multiplicative interferences of scatter. The models

254   were described by the error on test set samples. A summary of the calibration parameters

255   examined for PCR+ and PLS methods are presented in Table 2. Results show that the

256   multivariate methods achieved superior calibration correlations to the monovariable method,

257   with results further improved by SNV correction. The PCR+ quantification with SNV correction

258   yielded the best results, with calculated average sample error of 10.8% on values. Graphs for

259   individual components comparing specified *versus* estimated values are shown in Figure 6. The

260   calibrations using PCR+, PLS and PLS with SNV achieved sample errors 12.6%, 13.6% and

261   14.0% respectively. The differences between the six spectroscopic measurements of one sample

262   were found to be on average 9.6% of the components value after data manipulation. The limit of

263   detection for the Raman spectrometer is *ca* 2% or better.

264

265   **Quaternary quantification of Mg-Ca carbonate mixtures by XRD-PSD**

266

267   To further ascertain the accuracy of the calibration procedures, four samples of mixed powders

268   were quantitatively analysed by XRD. Diffraction patterns of these four mixtures are presented

269   in Figure 7. The least-squares fits were performed using the moderate-to-high 2θ range, because

270   for this region the PSD records patterns that represent diffraction from close-to-random

271   crystallite orientations for all the phases present. The lower-angle peaks were not used in the

272   fitting as they can arise from preferred orientation of crystallites in the mount and therefore their

273   intensities are less reliable for quantification purposes. Corrections for the effects of X-ray

274   absorption were applied using the mass absorption coefficients for each phase in the mixture in

275   order to convert from pattern fit proportions to weight percent values (Le Blond et al. 2009). The

276   XRD-PSD quantification yielded results with calculated average sample error of 14.06% on

277   values (Table 2). The peak intensity for hydromagnesite was significantly lower than the

278   intensities of the other carbonates. The quantifications by Raman spectroscopy and XRD-PSD

279   were compared to each other by error on sample values (Table 2). Both XRD and Raman

280   spectroscopy when combined with PLS showed *ca* 14% error on the component value. The

281   average error on values obtained by XRD-PSD was 14% and by Raman spectroscopy 10% and

282   20% for chemometric and monovariable methods respectively. Hence, the results show that both

283   analytical techniques are comparable and successfully quantify carbonate mixtures.

284

285   **Discussion**

286

287   While it is generally accepted that a linear relationship exists between Raman signal intensity

288   and concentration, the spectral intensity of the Raman shift also relates to several factors.

289   Notably, polarizability, molecular site symmetries, instrument variables, differences in particle

290   sizes and the degree of order in materials. Further, magnesium and calcium carbonates form

291   anisotropic crystals which can lead to broadening of peaks caused by longitudinal and transverse

292   splitting (White 1974), although results indicate that where the beam sampled area is 100μm

293   diameter and mode grain sizes are 4-7μm then the effects of anisotropic optical properties are

294   limited relative to the modal abundance of the constituent minerals within the sampled area.

295

296   It is evident that the fabricated mineral standards do not show the same Raman intensity. Given

297   that instrument settings remained constant throughout the analyses and that SEM and PSA

298   indicate fairly uniform particle size distributions, it is likely that differences in intensity stem

299 largely from differences in polarizability of the four mineral species, perhaps, with the intensity

300 increasing with increasing ratio of calcium to magnesium cations in the molecule. However other

301 additional effects may also apply. In the fabricated reference material spectra, the v_1 peak for

302 huntite shows a higher intensity than that of hydromagnesite (Figure 1b). Given that the synthetic

303 hydromagnesite is texturally comparable to natural hydromagnesite, and is devoid of spectral

304 evidence for short range disorder associated with rapid conditions of synthesis, available data

305 suggests that the principal causative factor for the differences in measured intensities for the two

306 mineral phases stems from a higher electron density in huntite during excitation, relative to

307 hydromagnesite.

308

309 The potential effect of particle size on Raman spectral intensity has been investigated in several

310 studies. However, the outcomes are still unclear and in some cases are in contradiction (Pellow-

311 Jarman et al. 1996). To further investigate the possible effect of particle size on Raman peak

312 intensity a separate experiment was undertaken in which dolomite was separated into five

313 different grain size fractions. The mode sizes of the fractions measured by PSA laser diffraction

314 were 145μm, 98μm, 56μm, 15μm and 2μm. The Raman spectra show that as the grain size

315 reduced to *ca* 56μm and with further grain size reduction the intensity decreases (Figure 8). The

316 Raman intensity increase was *ca* 15% in the 145-56μm sample range. The decrease in intensity

317 was somewhat smaller (*ca* 6%) in the 56-2μm sample size range. Hence, evidence suggests that

318 the Raman signal increases as the grain size decreases, but then subsequently the intensity

319 decreases with an increased proportion of very fine particles. One possible interpretation is that

320 the observed relationship registers a shift in relative contribution of particle sizes, packing and

321 surface defect concentration to the observed intensity. In the case of comparatively large

322   particles, the measured intensity reflects primarily the relative contribution of voids and particles.

323   With decreasing particle sizes (nm scale) the intensity decreases primarily as a function of high

324   defect concentrations in closely packed small particles.

325

326   **Concluding Remarks**

327

328   The findings show it is possible to use Raman to quantify quaternary carbonate mineral mixtures

329   with high accuracy. However, absolute values cannot be used if instrument variables are changed

330   and would require two-point recalibration for different spectrometers and experimental settings.

331   The multivariable chemometric methods gave better results than monovariable peak height

332   calibration. The most accurate results with respect to sample error were provided by the PCR+

333   SNV method. From multivariable models the calibration employing the PCR+ method achieved

334   lower sample error than that of the PLS method. The best calibration method was found to be

335   principle component regression with SNV correction applied. The sample error for this

336   quantification method was on average 10.8% of the component value. The monovariable linear

337   calibration method gave a strong calibration with R^2 = 0.9860, 0.9859, 0.9734 and 0.9505 for

338   huntite, hydromagnesite, dolomite and magnesite respectively. However independent samples

339   were measured with average sample error of 20% of component value. The spectral area of the

340   v_1 symmetrical stretching mode proves to be suitable for identification as well as for quantitative

341   work thanks to data manipulation software. Maximum height of the symmetric stretch mode has

342   also been used to assess the relative standard deviations of Raman measurements, ranging from

343   2.1-9.6% for one-component and four-component sample respectively. It needs to be stressed

344   that the latter includes error emerging from inhomogeneity of mixing. Single peak height

345   measurements offer a simple solution where complex mathematical models cannot be applied,

346   for example when dealing with spectra with abnormalities or fluorescence.

347

348   **Acknowledgements**

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353

354   **References**

355   Culka, A., Jehlicka, J., Vandenabeele, P. and Edwards, H.G.M. (2011) The detection of

356   biomarkers in evaporate matrices using a portable Raman instrument under Alpine conditions.

357   Spectrochimica Acta Part A, 80, 8-13.

358

359   Dandeu, A., Humbert, B., Carteret, C., Muhr, H., Plasari, E., and Bossoutrot, J.M. (2006)

360   Raman Spectroscopy – A Powerful Tool for the Quantitative Determination of the Composition

361   of Polymorph Mixtures: Application to $CaCO_3$ Polymorph Mixtures. Chemical Engineering&

362   Technology, 29, 221-225.

363

364   Edwards, H.G.M., Villar, S.E.J., Jehlicka, J., and Munshi, T. (2005) FT-Raman spectroscopic

365   study of calcium-rich and magnesium-rich carbonate minerals. Spectrochimica Acta A, 61, 2273-

366   2280.

367

368   Fevotte, G. (2007) In Situ Raman Spectroscopy for In-line Control of Pharmaceutical

369   Crystallization and Solids Elaboration Processes: A Review. Chemical Engineering Research &

370   Design, 85, 906-920.

371

372   Frost, R.L. and Dickfos, M.J. (2007a) Raman spectroscopy of halogen-containing carbonates.

373   Journal of Raman Spectroscopy, 38, 1516-1522.

374

375   Frost, R.L. and Dickfos, M.J. (2007b) Hydrated double carbonates – a Raman and infrared

376   spectroscopic study. Polyhedron, 26, 4503-4508.

377

378   Frost, R.L. (2011) Raman spectroscopic study of the magnesium carbonate mineral

379   hydromagnesite ($Mg_5[CO_3]_4(OH)_2].4H_2O$). Journal of Raman Spectroscopy, 42, 1690-1694.

380

381   Gunasekaran, S., Anbalagan, G. and Pandi, S. (2006) Raman and infrared spectra of carbonates

382   of calcite structure. Journal of Raman Spectroscopy, 37, 892-899.

383

384   Hollingberry, L.A. and Hull, T.R. (2010) The fire retardant behavior of huntite and

385   hydromagnesite – A review. Polymer Degradation and Stability, 95, 2213-2225.

386

387   Hopkinson, L.J., Rutt, K.J. and Cressey, G. (2008) The Transformation of Nesquehonite to

388   Hydromagnesite in the System $CaO-MgO-H_2O-CO_2$: An Experimental FT-Raman Spectroscopic

389   Study. The Journal of Geology, 116, 387-400.

390

391   Hopkinson, L.J., Kristova, P., Rutt, K.J., and Cressey, G. (2012) Phase transitions in the system

392   MgO-CO_2-H_2O during CO_2 degassing of Mg-bearing solutions. Geochimica et Cosmochimica

393   Acta, 76, 1-13.

394

395   Jehlicka, J., Vitek, P., Edwards, H.G.M., Heagraves, M., and Capoun, T. (2009) Application of

396   portable Raman instruments for fast and non-destructive detection of minerals on outcrops.

397   Spectrochimica Acta Part A, 73, 410-419.

398

399   Jehlicka, J., Culka, A., Vandenabeele P. and Edwards, G.M. (2011) Critical evaluation of a

400   handheld Raman spectrometer with near infrared (785nm) excitation for field identification of

401   minerals. Spectrochimica Acta Part A, 80, 36-40.

402

403   Kaabar, W., Bott, S. and Devonshire, R. (2011) Raman spectroscopic study of mixed carbonate

404   materials. Spectrochimica Acta Part A, 78, 136-141.

405

406   Kinsman, D.J.J. (1967) Huntite from a carbonate evaporite environment. American Mineralogist,

407   52, 1332-1340.

408

409   Le Blond, J.S, Cressey, G., Horwell, C.J., and Williamson, B.J. (2009) A rapid method for

410   quantifying single mineral phases in heterogeneous natural dusts using X-ray diffraction. Powder

411   Diffraction, 24, 17-23.

412

413   Lippmann, F. (1973) Sedimentary carbonate minerals, Springer, Berlin.

414

415   Noguchi, N., Shinoda, K., Masuda, K. (2009) Quantitative analysis of binary mixtures using

416   Raman micro-spectroscopy: Calibration curves for silica and calcium carbonate minerals

417   application to an opaline silica nodule of volcanic origin. Journal of Mineralogical and

418   Petrological Sciences, 104, 253-262.

419

420   Pakjamsai, C. and Suwanprateeb, J. (2000) Using FT-Raman spectroscopy for quantitative

421   determination of high filler content in particulated composites. Journal of Applied Polymer

422   Science, 78, 1947-1954.

423

424   Pellow-Jarman, M., Hendra, P.J., and Lehnert, R.J. (1996), The dependence of Raman signal

425   intensity on particle size for crystal powders. Vibrational Spectroscopy, 12, 257-261.

426

427   Rividi, N., van Zuilen, M., Philippot, P., Menez, B., Godard, G. and Poidaz, E. (2010)

428   Calibration of Carbonate Composition Using Micro-Raman Analysis: Application to Surface

429   Exploration. Astrobiology, 10, 293-309.

430

431   Scheetz, B.E. and White, W.B. (1977) Vibrational spectra of the alkaline earth double

432   carbonates. American Mineralogist, 62, 36-50.

433

434   Stamatakis, M.G. (1995) Occurrence and genesis of huntite-hydromagnesite assemblages,

435   Kozani, Greece: important new white fillers and extenders. Transactions of the Institution of

436   mining and metallurgy section B Applied Earth Science, 104, 179-186.

437   Vagenas, N.V. and Kontoyannis, C.G. (2003) A methodology for quantitative determination of

438   minor components in mineral based on FT-Raman spectroscopy The case of calcite in dolomitic

439   marble. Vibrational Spectroscopy, 32, 261-264.

440

441   Vandenabeele, P., Jehlicka, J., Vitek, P. and Edwards, H.G.M (2012) On the definition of Raman

442   spectroscopic detection limits for the analysis of biomarkers in solid matrices. Planetary and

443   Space Science, 62, 48-54.

444

445   Vagenas, N.V., Gatsouli, A. and Kontoyannis, C.G. (2003) Quantitative analysis of synthetic

446   calcium carbonate polymorphs using FT-IR spectroscopy. Talanta, 59, 831-836.

447

448   Vitek, P., Ali, E.M.A., Edwards H.G.M., Jehlicka, J., Cox, R. and Page, K. (2012) Evaluation of

449   portable Raman spectrometer with 1064nm excitation for geological and forensic applications.

450   Spectrochimica Acta Part A, 86, 320-327.

451

452   White, W.B., (1974), The carbonate minerals. In Farmer V.C., The Infrared spectra of minerals,

453   pp227-282, Mineralogical Society Monograph 4, London.

454

455   **FIGURES**

456

457   Figure 1: a) XRD-PSD patterns of the phases used to produce the mixtures, together with

458   identification fingerprints from the ICDD database and b) Raman spectra of the fabricated

459   reference materials.

460

461   Figure 2: Back-scattered scanning electron microscope images of: a) Dolomite reference

462   material, b) Huntite reference material, c) Synthetic hydromagnesite reference material, d)

463   Magnesite reference material, e) Aggregate of interspersed hydromagnesite and huntite platelets,

464   with concoidal fractured magnesite rhomb, marked with arrow (sample 9, Table 1), f) Aggregate

465   of micron-sized huntite plates, interspersed with similarly sized fragments of dolomite, alongside

466   a *ca* 1.4µm long residual coarse grained dolomite crystal, marked with arrow (sample 11, Table

467   1).

468

469   Figure 3: The particle size analysis by laser diffraction showing volume distribution profiles on

470   logarithmic scale of the four fabricated reference materials. See text for details.

471

472   Figure 4: a) Representative Raman spectra of mixed carbonate powders sample 1, sample 4,

473   sample 10, sample 18 (Table 1) where abbreviated labelling is as follows: H = huntite, HM =

474   hydromagnesite, D = dolomite and M = magnesite. b) Detail of curve fitting for Raman spectra

475   after deconvolution in the range 1130-1080cm^{-1} (sample 1, Table 1). c) Detail of curve fitting for

476   Raman spectra after deconvolution in the range 1130-1080cm^{-1} (sample 10, Table 1).

477

478   Figure 5: Calibration graphs for monovariable method in absolute values plotted against weight

479   fraction: a) Hydromagnesite - peak height at *ca* 1118cm^{-1}, b) Huntite - peak height at

480   *ca* 1122cm^{-1}, c) Dolomite - maximum peak height at *ca* 1097cm^{-1}, d) Magnesite - peak height at

481   *ca* 1094cm^{-1}(diamonds) and at *ca* 331cm^{-1} (triangles).

482

483   Figure 6: Calibration graphs for PCR+ method with SNV correction applied showing estimated

484   *versus* specified values (solid diamonds) with XRD-PSD data superimposed (open circles): a)

485   Hydromagnesite, b) Huntite, c) Dolomite and d) Magnesite.

486

487   Figure 7: XRD-PSD patterns of selected mixtures (samples 1, 2, 3, and 18) together with

488   identification fingerprints from the ICDD database (Table 1).

489

490   Figure 8: Particle size effect on Raman intensity of dolomite, plotted as peak height ratio I/I_{max}

491   (i.e. measured intensity/maximum intensity measured from 56 μm particle size fraction) against

492   particle size.

493

494   Table 1: Mixture composition as weight in weight percentage [%] - minerals were weighed on an

495   analytical balance to 0.01mg for one gram samples giving an error 0.001%.

496

497   Table 2: Assessment of quantitative calibration models for quaternary mixture where RS =

498   Raman spectroscopy, PCR+ = principal component regression, PLS = partial least squares, XRD

499   = X-ray diffraction and SNV = standard normal variation.

500

501

502

Sample	Dolomite [%]	Magnesite [%]	Huntite [%]	Hydromagnesite [%]
1	12.07	7.96	15.06	64.92
2	-	5.02	92.96	2.02
3	12.05	-	-	87.95
4	8.02	11.92	50.07	29.99
5	2.02	3.96	32.10	61.93
6	14.03	2.00	62.04	21.93
7	15.99	-	84.01	-
8	-	16.09	-	83.91
9	6.01	14.01	69.97	10.01
10	10.01	9.96	39.94	40.09
11	7.87	12.09	70.24	9.80
12	4.00	6.01	-	89.99
13	-	-	25.79	74.21
14	-	-	50.29	49.71
15	14.93	4.27	-	80.80
16	5.98	15.98	78.04	-
17	-	2.12	4.02	93.86
18	13.85	5.13	10.95	70.08
19	-	-	100	-
20	-	-	-	100

503

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Analytical method	Calibration method	Correction	Error on values [%]
RS	PCR+	none	12.6
RS	PCR+	SNV	10.3
RS	PLS	none	13.6
RS	PLS	SNV	14.0
RS	monovariable	none	20.0
XRD-PSD	least-squares fitting	absorption	14.1

507

[A]

huntite

hydromagnesite

dolomite

magnesite

[84-820] huntite

[70-1177] hydromagnesite

[73-2361] dolomite

[86-2344] magnesite

°2θ

[B]

[A] Dolomite

[B] Huntite

[C] Hydromagnesite

[D] Magnesite

[E] Sample 9

[F] Sample 11

[A] $y = 287.93x - 1526.3$
$R^2 = 0.9860$

[B] $y = 540x + 2774.4$
$R^2 = 0.9859$

[C] $y = 1156.2x + 1186.5$
$R^2 = 0.9734$

[D] $y = 236.9x + 948.02$
$R^2 = 0.9505$

$y = 173.26x + 184.97$
$R^2 = 0.9727$

sample 1

sample 2

sample 3

sample 18

[84-820] huntite

[70-1177] hydromagnesite

[73-2361] dolomite

[86-2344] magnesite

°2θ