Sulfur Isotope Measurement of Sulfate and Sulfide by High-Resolution MC-ICP-MS

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1   **Abstract**

2

3   We have developed a technique for the accurate and precise determination of $^{34}S/^{32}S$ isotope

4   ratios ($\delta^{34}S$) in sulfur-bearing minerals using solution and laser ablation multiple-collector

5   inductively coupled plasma mass spectrometry (MC-ICP-MS). We have examined and

6   determined rigorous corrections for analytical difficulties such as instrumental mass bias,

7   unresolved isobaric interferences, blanks, and laser ablation- and matrix-induced isotopic

8   fractionation. Use of high resolution sector-field mass spectrometry removes major isobaric

9   interferences from O_2^+. Standard–sample bracketing is used to correct for the instrumental mass

10   bias of unknown samples. Blanks on sulfur masses arising from memory effects and residual

11   oxygen-tailing are typically minor (< 0.2 ‰, within analytical error), and are mathematically

12   removed by on-peak zero subtraction and by bracketing of samples with standards determined at

13   the same signal intensity (within 20 %). Matrix effects are significant (up to 0.7 ‰) for matrix

14   compositions relevant to many natural sulfur-bearing minerals. For solution analysis, sulfur

15   isotope compositions are best determined using purified (matrix-clean) sulfur standards and

16   sample solutions using the chemical purification protocol we present. For in situ analysis, where

17   the complex matrix cannot be removed prior to analysis, appropriately matrix-matching

18   standards and samples removes matrix artifacts and yields sulfur isotope ratios consistent with

19   conventional techniques using matrix-clean analytes. Our method enables solid samples to be

20   calibrated against aqueous standards; a consideration that is important when certified,

21   isotopically-homogeneous and appropriately matrix-matched solid standards do not exist.

22   Further, bulk and in situ analyses can be performed interchangeably in a single analytical session

23   because the instrumental setup is identical for both. We validated the robustness of our analytical

24   method through multiple isotope analyses of a range of reference materials and have compared

25   these with isotope ratios determined using independent techniques. Long-term reproducibility of

26   S isotope compositions is typically 0.20 ‰ and 0.45 ‰ (2σ) for solution and laser analysis,

27   respectively. Our method affords the opportunity to make accurate and relatively precise S

28   isotope measurement for a wide range of sulfur-bearing materials, and is particularly appropriate

29   for geologic samples with complex matrix and for which high-resolution in situ analysis is

30   critical.

31

32   *Keywords*

33   Sulfur, Isotope Composition, ICP, Mass Spectrometry, Laser Ablation

1. Introduction

Sulfur is widely distributed throughout the environment. Principally, sulfur occurs as sulfate in open, oxygenated seawater, while H_2S and other reduced sulfide species reside in anoxic basins and sediment porewaters. In sediments, igneous and metamorphic rocks and metal-rich ore deposits, sulfur occurs in various oxidation states, such as sulfate, elemental sulfur and numerous metal sulfides. Variations in sulfur isotopic compositions of these reservoirs can be large (on the order of $\delta^{34}S \sim 20 - 50$ ‰ (Faure, 1986; Hoefs, 1997)) and so they serve as key tracers of sources and cycling of sulfur species in biological and geochemical processes (Thode et al., 1961; Goldhaber and Kaplan, 1974; Ohmoto and Rye, 1979; Canfield, 2001; Shanks, 2001).

Conventionally, measurements of sulfur isotope ratios are performed using gas-source mass spectrometry (GS-MS) in which sulfur is introduced as gaseous SO_2 or SF_6 (Thode et al., 1961; Fritz et al., 1974; Robinson and Kusakabe, 1975; Rees, 1978). The latter is preferred for high-precision S isotope analysis because SF_6 has no spectral interferences from oxygen species and no memory effects (Rees, 1978). However, sample preparation for GS-MS is complex and time-consuming (Thode et al., 1961). Online elemental-analyzer isotope-ratio mass spectrometry (EA-IRMS) has been more recently developed to automate the combustion formation and chromatographic purification procedures for a SO_2 gas source (Giesemann et al., 1994; Grassineau et al., 2001; Studley et al., 2002) and is now a widely-used technique for sulfur isotopic measurements. This approach has reduced minimum sample mass requirements (< 1 mg S) and expedited sample throughput. For GS-MS, $\delta^{34}S$ ratios are commonly determined on masses 66 ($^{34}S^{16}O_2^+$) and 64 ($^{32}S^{16}O_2^+$). Variations of $^{18}O/^{16}O$ contributing to the isotopic

57   composition of the SO$_2$ analyte are often not reproducible and poorly constrained using

58   automated preparation systems and have resulted in calculated δ^{34}S values in error by up to $1 - 3$

59   ‰ (Fry et al., 2002). Thus, manual preparation of SO$_2$ is still required in many cases in order to

60   obtain the necessary precision and accuracy for S isotope analysis. A procedure that minimizes

61   sampling handling and accelerates analysis, but enables high-precision isotope measurements, is

62   highly desirable.

63

64   Alternative methods, such as ion microprobe (Chaussidon et al., 1987; Eldridge et al., 1987;

65   Paterson et al., 1997; Mojzsis et al., 2003) and laser probe coupled to GS-MS (Shanks et al.,

66   1998; Hu et al., 2003) have been developed for in situ measurement of S isotopes at increased

67   spatial resolution to obtain information about biogeochemical processes that cannot be gained

68   through bulk analytical measurements. These techniques alleviate the need for extensive sample

69   preparation and so reduce minimum sample size and expedite sample throughput. However, they

70   are subject to shortcomings including significant instrumental mass bias resulting from matrix

71   effects. Consequently, it is necessary to have isotopically homogeneous and well-characterized,

72   matrix-matched mineral standards, which are not available for all materials (Paterson et al.,

73   1997; Riciputi et al., 1998). Multiple-collector thermal ionization mass spectrometry (MC-

74   TIMS) has also been examined to measure precise S isotope ratios (Mann and Kelly, 2005). The

75   use of a sulfur double-spike as an internal standard for MC-TIMS alleviates the need for

76   homogeneous, matrix-matched external standards (Mann and Kelly, 2005). This method allows

77   precise determination of S isotope ratios at small sample sizes (< 100 μg S). However, the

78   addition of the double-spike technique requires the sample be in solution form and so the

79   benefits of in situ analysis without sample preparation are lost.

80

81 Inductively coupled plasma mass spectrometry (ICP-MS) is increasingly becoming used as a tool

82 for the measurement of stable isotope systems (Halliday et al., 1998; Albarède and Beard, 2004;

83 Anbar and Rouxel, 2007). ICP-MS instruments are compatible with numerous sample

84 introduction schemes, including solution (*bulk*) analysis and laser-ablation (*in situ*) analysis,

85 which are not available for other techniques. ICP-MS represents a promising technique for the

86 analysis of sulfur isotopes at sample masses (~ 10 µg S) similar to other techniques (Menegário

87 et al., 1998; Mason et al., 1999; Prohaska et al., 1999; Krupp et al., 2004; You and Li, 2005;

88 Clough et al., 2006; Mason et al., 2006). Measurement of S isotopes by single-collector ICP-MS

89 is obtained sequentially and vriability of plasma conditions (e.g., efficiency of ionization, ion

90 beam extraction) can significantly degrade the measurement of isotope ratios. The overall

91 precision achievable by this method is typically greater than 2 to 5 ‰ (Jarvis et al., 1992;

92 Menegário et al., 1998; Evans et al., 2001) and is not sufficient to resolve all sulfur isotope

93 variations occurring in nature. The introduction of multiple collector ICP-MS technology has

94 enabled simultaneous measurement of multiple isotopes, providing precise and rapid isotope

95 ratio determination. Precision better than 1 ‰ is now obtainable for $\delta^{34}S$ isotope ratios (Clough

96 et al., 2006; Mason et al., 2006). Implicit in the accurate and precise determination of isotope

97 ratios by MC-ICP-MS is an appropriate correction for instrumental mass discrimination. To date,

98 external normalization (Rehkämper and Halliday, 1998; Maréchal et al., 1999) using either

99 $^{37}Cl/^{35}Cl$ or $^{30}Si/^{29}Si$ isotope spikes has been preferred for S isotopes studies (Clough et al., 2006;

100 Mason et al., 2006). However, it has not been sufficiently demonstrated that external

101 normalization is appropriate for mass bias correction for all sulfur-bearing samples with a range

102 of matrix, particularly for laser ablation MC-ICP-MS where the matrix cannot be removed prior

103   to analysis. Our limited understanding of the effects of matrix for S isotope determination greatly

104   limits the current application of solution and laser ablation MC-ICP-MS .

105

106   Development of a new analytical technique for sulfur isotope measurement is motivated by the

107   need for rapid, versatile, precise and accurate *in situ and bulk* characterization of *sulfate* (e.g.,

108   anhydrite, barite, gypsum) *and sulfide* minerals (e.g., pyrite, chalcopyrite), widespread in the

109   environment. Here, we present a detailed description of sulfur isotope measurement of sulfate

110   and sulfide by solution and laser-ablation MC-ICP-MS. We examine potential difficulties

111   associated with this technique, including instrumental and laser-ablation induced mass

112   fractionation, isobaric interferences, blank contributions and matrix effects, and detail

113   approaches to correct for these artifacts, enabling higher-precision measurements. This new

114   contribution affords the possibility to carry out accurate and precise S isotope measurements for

115   a range of sulfur-bearing materials both by bulk analysis and in situ at sub-millimeter spatial

116   scales and should be of interest to a variety of geological and geochemical studies.

117

118   **2. Analytical Methods**

119

120   *2.1. Preparation of reagents, standards and blanks*

121   All bottles and vials used for sample preparation and storage were cleaned for a 24 h period in

122   Fisher TraceMetal grade 20 % hydrochloric acid and rinsed three times with 18 MΩ cm Milli-Q

123   water. All standard and sample solutions were prepared for analysis as matrix-matched, purified

124   S solutions stabilized in 2 % (w/w) nitric acid (HNO$_3$). Either SeaStar Baseline^{TM} (SeaStar

125   Chemicals Inc., Sidney, BC Canada) or Fisher Optima^{TM} (Fisher Scientific Co., Agawam, MA)

126   ultra-pure HNO_3 was used. Milli-Q water used for dilutions was prepared using a Millipore

127   Element de-ionizing unit operated at 18 MΩ cm.

128

129   Sulfur reference materials IAEA-S-1, S-2, S-4 and NBS-123 (Coplen and Krouse, 1998; Ding et

130   al., 2001; Qi and Coplen, 2003) were used to calibrate laboratory (in-house) standards and to

131   enable inter-laboratory comparison against the V-CDT scale. Laboratory standard solutions

132   (S_{Alfa} and S_{Spex}) containing 20 ppm S were prepared from high-purity solutions and used

133   throughout daily analytical sessions as the isotope reference. S_{Alfa} was prepared by gravimetric

134   dilution of an AlfaAesar Specpure^{TM} 1000 µg ml^{-1} S stock (Alfa Aesar, Johnson-Matthey Co.,

135   Ward Hill, MA) and S_{Spex} by gravimetric dilution of a Spex CertiPrep$^{®}$ 10,000 µg ml^{-1} S stock

136   (SPEX CertiPrep Group, Metuchen, NJ). In addition, a range of geological reference samples

137   with known isotope compositions were used as reference materials to enable comparison against

138   isotope ratios determined using conventional analytical techniques. Two percent HNO_3 blank

139   solutions were prepared from the same lot to quantify sulfur blanks throughout analytical

140   sessions.

141

142   A mineral standard of anhydrite ($CaSO_4$; hereafter referred to as Sch-M-2) was prepared for laser

143   ablation and bulk analysis in order to cross-calibrate solution and laser techniques. The Sch-M-2

144   solution was prepared by dissolving an appropriate mass of pure anhydrite in Milli-Q water and

145   stabilizing the solution in ultra-pure 2 % HNO_3 acid to obtain a standard containing 20 ppm S.

146   For laser ablation analysis, a 2 mm thick section was cut, polished and mounted onto a standard

147   (45 x 25 mm) petrographic slide; no further preparation was necessary.

148

149 *2.2. Chemical purification of reference standards and sulfide-sulfate samples*

150 Less than 50 mg of sample was accurately weighed into a 15ml PTFE digestion vessel. Samples

151 were first reacted with 5 ml of HNO_3 (50 %) and taken to dryness on hot plate at less than 70 °C.

152 Total digestion of the dry residue (containing abundant elemental sulfur) was obtained using 3

153 ml of concentrated HNO_3 and 2 mL of HCl (50 %). The solution was heated in the sealed PTFE

154 container on a hot plate at a temperature of 70 °C and taken to dryness. The dry residue was fully

155 dissolved with 4 mL of 2 % HNO_3. During dissolution of Ag_2S, insoluble white crystalline solids

156 (presumably AgCl) precipitated and were separated from the solution by centrifugation.

157

158 A precise solution volume, corresponding to 500 μg of S, was then purified on a cation exchange

159 chromatographic column AG50-X8 (H^+ form, Biorad, Hercules, CA, USA). The column was

160 filled with 2.5 ml of resin (wet volume) and washed with 20 mL H_2O and conditioned with 10

161 mL 1.4N HNO_3. The solution that passed through the column contains S and other oxyanions

162 (e.g., silicic acid, phosphate, molybdate) whereas matrix elements (including sulfide- and sulfate-

163 forming elements Fe, Ca, Cu, Zn) are strongly adsorbed on the resin. Complete recovery of S is

164 assured after washing the column with 5 ml of 2 % HNO_3. The final solution was diluted with an

165 appropriate amount of 2 % HNO_3 to obtain a final stock containing 50 ppm S.

166

167 Quantitative recovery of S is essential to avoid potential isotope fractionation of standards and

168 samples during chemical processing. Loss of S can arise from volatilization of H_2S, or from the

169 formation of insoluble sulfate or elemental sulfur. The former is unlikely as the use of strong

170 oxidizing acids (HNO_3) during sample dissolution prevents the formation of volatile H_2S.

171 Further, complete and repeated dissolution of sulfur-bearing particles is assured prior to column

172   purification. Dissolution yields were evaluated for pyrite by measuring Fe/S ratios in solution

173   prior to S purification. In all instances, molar S/Fe ratios in solutions were 1.95 ± 0.05, consistent

174   with pyrite stoichiometry and indicate no loss of S. Complete recovery of S during column

175   purification is ensured by passing S as sulfate through the AG50-X8 resin and washing with 5 ml

176   of 2 % HNO_3. Yields of S are 98 ± 4 %, as calculated from purification of multiple, independent

177   aliquots of the S_{Alfa} in-house standard doped with matrix elements. The measured isotope

178   compositions of the resulting purified standards are consistent within analytical uncertainties (see

179   section 3.3). The procedural blank, resulting from chemical processing and purification is ~ 0.05

180   % (~ 0.25 µg per 500 µg S used for column chemistry).

181

182   *2.3. Instrumentation and apparatus*

183   Isotopic measurements were performed using a NEPTUNE multiple collector inductively

184   coupled plasma mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with

185   nine Faraday Cups. A NewWave UP213 Nd:YAG laser was used as the ablation source for

186   analysis of solid samples. Instrument settings and typical operating parameters are summarized

187   in Figure 1 and Table 1. Sulfur solutions are aspirated using Ar as the nebulizer gas. A laser

188   ablation cyclonic spray dual chamber (a.k.a. Stable Sample Introduction System) and PFA-50

189   nebulizer (both from Elemental Scientific Inc., Omaha, NE) were used to introduce aerosols to

190   the ICP torch. This spray chamber hosts an additional inlet to allow introduction of ablated

191   material to the torch. The laser is connected directly to the spray chamber via 3 mm internal

192   diameter Tygon tubing and uses He as the carrier gas from the laser to the ICP. The setup is such

193   that laser ablation and solution aspiration can be operated simultaneously and enables laser

194   particles to be efficiently mixed with an ultra-pure 2 % HNO_3 blank solution prior to injection

195   into the ICP torch. Thus, laser particles are effectively analyzed as a 'wet plasma' ensuring that

196   ablated aerosols are closely matrix-matched to solution standards. We opt not to use 'dry' plasma

197   conditions (Mason et al., 2006) because this limits the application of the method to in situ

198   analysis only. Sulfur is highly volatile and, therefore, passing solutions through a desolvating

199   nebulizer to obtain dry plasma conditions is not viable for bulk analysis. Our setup allows for

200   interchangeable bulk and in situ S isotope measurement.

201

202   Operating parameters for laser analysis are optimized in order to provide the most stable signal

203   intensities during ablation. The laser is operated in apertured mode, with a spot size of 60 μm

204   and a minimum total signal intensity of 10 volts (^{32}S signal). The power output of the laser is

205   adjusted so as to ensure that the signal intensity of the ablated sample and bracketing solution

206   standard are the same, typically with less than 20 % difference. A line scan ('raster') protocol is

207   used in preference to a single crater mode in order to obtain a higher and more uniform rate of

208   material removal with respect to time. The raster mode utilizes a movable sample stage under a

209   fixed laser beam to generate the desired raster pattern. The size of the trench formed during

210   ablation is ~ 200 x 100 μm in cross-sectional area and ~ 250 μm deep. A scan speed of 5 μm s^{-1}

211   is used during ablation and yields an ablation removal rate for the sample of ~ 60 ng s^{-1}. Total

212   acquisition time is ~ 4 minutes and results in ablation of ~ 15 μg of sample. The signal intensity

213   is monitored to ensure that transport of sample into the ICP-MS does not significantly diminish

214   as material is ablated during analysis.

215

216   *2.4. Isotope measurement and data acquisition*

217 Isotope ratio measurements are performed in high mass resolution mode in order to separate

218 sulfur from potential interfering species (Table 2). Isotopic measurements are performed on

219 masses ^{32}S, ^{33}S and ^{34}S. Molecular interferences from ^{16,17,18}O$_2$ are heavier than elemental

220 species, so isotopes of sulfur are determined free from molecular interferences on the low mass

221 shoulder of interfering species (Figure 2). Data are not reported for ^{36}S because of the low

222 abundance of this isotope and interferences from Ar.

223

224 Each measurement consists of twenty cycles, each cycle having 8.5 second integration. Data

225 acquisition for in situ analyses is initiated approximately 15 seconds after the laser is fired. This

226 delay accounts for transport of ablated material into the mass spectrometer and the time taken to

227 establish a stable signal on the Faraday cups. Similarly, data acquisition for solution analyses

228 begins once a stable signal is established for the aspirated sample. Baseline intensities are

229 measured for 5 seconds at the beginning of each analysis by deflecting the ion beams.

230 Background interference is evaluated by measuring signal intensities on sulfur masses whilst

231 aspirating blank (2 % nitric acid) solutions periodically throughout the analytical session (i.e.,

232 on-peak zero). On-peak background is measured on the low mass shoulder (identical to sample

233 measurements) to avoid tailing from O$_2$ and negative background due to possible ion scattering

234 on the sides of the Faraday Cup. Wash-out times of two minutes and four minutes are used

235 following solution and laser ablation analysis, respectively (Table 2). Automatic rejection of

236 outlying cycles (2σ outlier criterion) offered within the NEPTUNE software is not performed.

237 All data acquired, including raw Faraday intensities, raw measured isotope ratios and

238 corresponding standard deviations and standard errors for each measurement, are evaluated off-

239 line.

240

241   Absolute S isotope ratios of unknown samples are determined using standard-sample bracketing

242   (Belshaw et al., 1998; Albarède and Beard, 2004). The true S isotope ratio is calculated by

243   correction for instrumental mass bias by linear interpolation between the biases calculated from

244   two neighboring standard analyses. Isotope compositions are presented in the conventional delta

245   (δ) notation by reference to in-house matrix-matched standards (S_{Spex} and S_{Alfa}), i.e.;

246

247    $$\delta^{34}S = \left(\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{standard}} - 1 \right) \times 1000$$

248

249   Analogous relations are used for the determination of $\delta^{33}S$, substituting ^{33}S for ^{34}S in the

250   equation above. The isotope compositions of in-house standards used to bracket unknown

251   samples have been calibrated exactly against reference material IAEA-S-1. The S isotope

252   compositions of samples are then normalized to the Vienna Cañon Diablo Troilite (V-CDT)

253   scale assuming, by definition, $\delta^{34}S_{V-CDT}$ of IAEA-S-1 exactly equal to -0.3 ‰ (Ding et al.,

254   2001). Further calibration and verification of the 'accuracy' of the S isotope compositions of in-

255   house standards was examined by determining the isotope compositions of other reference

256   materials analyzed as unknowns. Within uncertainty, the isotope compositions of reference

257   materials determined by this study are consistent with published consensus $\delta^{34}S$ values (Table 3).

258   For individual analyses, internal precision is reported at the 1σ error level. For replicate analyses,

259   external reproducibility is reported at the 2σ error level.

260

261   **3. Experimental Results**

262

263 *3.1. Isobaric interference and background correction*

264 Isobaric interferences and blank contamination can contribute to measured signal intensities on

265 sulfur isotope masses of interest and can bias measured isotope ratios. An assessment of these

266 two artifacts is required in order to obtain the necessary precision and accuracy for S isotope

267 measurements. Isobaric interferences include molecular ions (e.g., ^{16}O-$^{16}O^+$, ^{32}S-$^1H^+$ and ^{17}O-

268 ^{16}O-$^1H^+$) and less abundant doubly-charged ions (e.g., $^{64}Zn^{2+}$) and exist on all isotopes of interest

269 (Table 2). For accurate determination of S isotope ratios, it is essential that these interferences

270 either be removed completely or be resolved with appropriate mass resolution. For the

271 NEPTUNE, sulfur isotope measurements can be performed setting the entrance slit to medium or

272 high resolution (high resolution recommended) and detector slit to low resolution. In this

273 configuration, sulfur is resolved as a flat plateau (peak shoulder) on the low mass side of

274 interfering oxygen species and the detector is positioned on this interference-free shoulder for

275 data collection (Figure 2). The mass resolution for this setup is defined by the resolving power of

276 the mass spectrometer, $m/\Delta m^*$ (Weyer and Schwieters, 2003). It is important to note that the

277 resolving power ($m/\Delta m^*$) is distinct to standard mass resolution given by the 10 % valley

278 definition, and is a factor of $3 - 4$ higher than standard mass resolution (Weyer and Schwieters,

279 2003). A resolving power $m/\Delta m^* \sim 5000 - 6000$ is sufficient to separate major oxygen

280 interferences, including contributions from oxygen-tailing and ion-scattering, from sulfur

281 isotopes of interest.

282

283 The resolving power of the NEPTUNE is not sufficient to fully separate sulfur from hydride

284 interferences ($m/\Delta m^* > 12,000$), and so hydride formation should be quantified. We calculate on

285 average $\sim 0.05 - 0.10$ % production efficiency for sulfur hydride. For the low abundance isotope

286 ^{33}S, contribution from ^{32}S-^{1}H is more than 10 % of the total signal on mass 33, resulting in

287 significant bias of the measured isotope ratio and poor reproducibility of δ^{33}S ratios of about 2 –

288 3 ‰ (see section 3.2.). Hydride contribution from ^{33}S-^{1}H^{+} on mass 34 is negligible (< 0.02 %)

289 and does not limit the overall precision for ^{34}S/^{32}S ratios obtainable by this technique, in

290 particular because the effect of hydride formation is corrected by the standard-sample bracketing

291 technique. The rate of hydride formation is calculated for each measurement using (^{33}S +

292 ^{32}SH)/^{32}S vs. ^{34}S/^{32}S relationship to ensure that hydride formation is uniform between sample and

293 standard analysis.

294

295 Blank contributions can include sulfur due to laboratory contamination and from instrument

296 memory. Previous high-precision S isotope ratio measurements by laser ablation lacked

297 quantitative assessment of blanks (Mason et al., 2006). The procedural blank for our purification

298 method was assessed during preparation and chemical purification of sulfur standards and

299 samples. The blank is calculated to be ~ 0.05 % of total sulfur processed. Typically, sulfur

300 intensities of the procedural blank are minor as compared to sulfur intensities of standards and

301 samples (~ 30 mV for blank *versus* 15 – 20 V for standard, on mass 32). Further, sulfur

302 contamination can result from transient memory effects during sulfur isotope measurement.

303 These effects are manifest as small, but variable, spikes in the sulfur intensity during the

304 aspiration of a blank solution after analysis of a sulfur-bearing analyte. Memory effects are not

305 significant for solution-based analysis and are removed by applying a two minute wash-out

306 period after solution analysis. However, they can be more important for laser ablation analysis

307 because residual particles can be carried from the laser cell to the mass spectrometer for an

308 extended period after ablation and isotope analysis have finished. Typically, a four minute wash-

309   out period after in situ analysis is sufficient and recommended to enable spikes arising from

310   residual particles to be removed.

311

312   Total background corrections are necessary if trace, but measurable, sulfur contamination or

313   unresolved interferences contribute to signal intensities and bias isotope compositions. Repeated

314   analyses of in-house sulfur standards at a range of sulfur concentration and signal intensity

315   indicate significant deviation of measured S isotope ratios from true ratios at low sulfur

316   concentration (Figure 3). Correction for total background is performed by periodic aspiration and

317   isotopic measurement of blank solutions throughout each analytical session. Absolute signal

318   intensity of the background is $\sim 30 - 50$ mV (on ^{32}S). Average background intensities are

319   determined for each isotope (on-peak zero) and are directly subtracted from the signal intensity

320   for each sulfur isotope mass as part of off-line evaluation. For routine sample analysis, the

321   necessary correction for background contributions is typically small (≤ 0.4 ‰), but can be

322   variable. However, these deviations are statistically significant and can produce perturbations of

323   S isotope ratios greater than 1.0 ‰ at less than one volt signal intensity (on ^{32}S). Approaches to

324   minimize the magnitude of the background correction required to within limits of analytical

325   precision are advantageous because the concentration and isotopic composition of the blank are

326   inherently variable and difficult to characterize. Accordingly, the following procedures are

327   recommended; (1) measure isotope ratios of standard and sample analytes at minimum signal

328   intensities ~ 10 volts (signal-to-background ratios > 300) and, (2) determine isotope

329   compositions of unknown samples with a standard analyzed at the same intensity (within ~ 20

330   %). By closely matching signal intensities, the mass bias calculated for the standard accounting

331   for effects of both instrumental fractionation and background can be directly applied to unknown

332   samples.

333

334   *3.2. Internal precision and instrument mass bias*

335   In this study, we choose to apply the standard-sample bracketing technique to correct for

336   instrumental mass discrimination. A matrix-matched sulfur solution is used as the bracketing

337   standard for both bulk and in situ sample analysis. The magnitude and stability of instrumental

338   mass bias is calculated from the evolution of the isotopic standard throughout the analytical

339   session. For sulfur, we calculate typical mass bias between 4.0 and 5.1 % per atomic mass unit.

340   Mass bias is variable between analytical sessions, but is generally stable to around 0.1 % over the

341   duration of a single session and to $0.01 - 0.02$ % between consecutive bracketing standards. The

342   stability of this mass bias determines the ultimate precision obtainable by the standard-sample

343   bracketing technique. Varying instrumental mass bias (i.e., drift) will increase the errors

344   associated with applying mass bias corrections to unknown samples and will compromise

345   analytical precision. We have assessed instrumental drift and observe no statistically significant

346   deviation of isotope ratios (> 0.02 %) during routine analysis of individual samples, for analysis

347   times up to approximately four minutes. Long-term drift, occurring over the duration of multiple

348   sample analyses, is easily corrected by stringent standard-sample bracketing of unknown samples

349   with standards analyzed immediately before and after. Data that show clear and large mass bias

350   drift (greater than ~ 0.5 ‰) during individual samples should be discarded.

351

352   The overall precision of bulk S isotope analysis using standard-sample bracketing has been

353   assessed from the long-term reproducibility of S_{Spex} and S_{Alfa} standard solutions measured over

354   multiple, independent analytical sessions (Figure 4). For routine bulk analysis, we estimate an

355   external precision of $\pm$ 0.21 ‰ (2σ) and $\pm$ 0.18 ‰ (2σ) for $\delta^{34}S_{Alfa}$ and $\delta^{34}S_{Spex}$, respectively (20

356   – 30 replicates). In contrast, the precision for $\delta^{33}S$ values deteriorate by an order of magnitude

357   relative to $\delta^{34}S$ due to the large contribution and high variability of unresolved ^{32}S-^{1}H

358   interference on ^{33}S (Figure 4). The external precision of in situ S isotope analysis is more

359   difficult to assess because real isotopic heterogeneity may contribute to variability of isotope

360   compositions determined by repeat analyses of mineral samples. An estimate of external

361   precision of in situ techniques was determined by replicate analysis of the isotopically

362   homogenous anhydrite standard Sch-M-2 and calculated to be $\pm$ 0.45 ‰ (2σ; 12 replicates).

363

364   *3.3. Matrix effects*

365   Instrumental mass bias within ICP-MS results from so-called 'space-charge' and 'ion-diffusion'

366   effects on the transmission of ionized particles (Tanner, 1992; Vanhaecke et al., 1993; Maréchal

367   et al., 1999) and has been shown to be sensitive to matrix composition (Galy et al., 2003;

368   Pietruszka et al., 2006). In order to evaluate the possibility of matrix effects from elements that

369   are commonly found in sulfide and sulfate minerals, we performed doping experiments using

370   S_{spex} standard solution mixed with various high-purity element solutions. For each experiment,

371   we used synthetic solutions with a matrix corresponding to stoichiometry of various sulfide and

372   sulfate minerals (e.g. anhydrite, pyrite, chalcopyrite, sphalerite, etc.). The S isotope ratios of

373   doped S_{spex} solutions were determined and compared against the S isotope ratio of purified S_{spex}

374   solutions (Figure 5). The results show, in most cases, that matrix effects from Ca, Fe, Ni, Mo, Sn

375   are significant (up to 0.7 ‰) and yield poorly reproducible isotope determination. The data also

376   indicate that the presence of matrix elements tend to increase the instrumental mass bias for S.

377

378   In order to evaluate the efficiency of the chemical purification procedure to remove matrix

379   elements, we separated and purified an aliquot of the doped solutions. The aliquots were

380   processed through cation-exchange (AG50-X8) resin as described previously and re-analyzed as

381   unknown samples. The results demonstrate that chemical purification effectively removes the

382   matrix and enables consistent and reproducible isotope measurements free of matrix effects

383   (Figure 5). Further, the data indicate that the chemical purification procedures do not introduce

384   any artificial isotope fractionation (e.g., from loss of S) that would compromise the accuracy of

385   this method. The only exception is Mo, which is not separated from S through the AG50-X8

386   resin. Thus, we conclude that this method is adequate for measuring most common sulfide and

387   sulfate minerals, except Molybdenite.

388

389   *3.4. Laser ablation parameters*

390   In situ analysis using laser ablation coupled to ICP-MS has been successfully developed and

391   applied for both elemental and isotope ratio measurements of geologic materials (Jackson et al.,

392   1992; Fryer et al., 1995; Horn et al., 2000; Russo et al., 2001; Košler et al., 2005; Mason et al.,

393   2006; Woodhead et al., 2007). To date, most applications have used nanosecond lasers for

394   sample ablation. These are recognized as introducing laser-induced fractionation, which are

395   superimposed on mass fractionation of the ICP-MS. Potential sources of elemental and isotopic

396   fractionation appear to be similar and include, (1) differential evaporation and/or condensation of

397   particles at the site of ablation, (2) variation of particle transport toward the ICP and, (3)

398   incomplete vaporization and ionization of particles in the ICP (Outridge et al., 1997; Eggins et

399   al., 1998; Figg et al., 1998; Horn et al., 2000; Jackson and Günther, 2003; Horn and von

400   Blanckenburg, 2007). In addition, differences between matrices of the ablated sample and

401   standard aerosols can introduce further mass discrimination and inaccurate mass fractionation

402   correction of ablated samples. In order to obtain the most precise and consistent isotope

403   measurements, it is essential to recognize and minimize mass discrimination introduced by the

404   laser to within the analytical uncertainties achievable by this method. Optimization of laser

405   protocols to minimize laser-induced fractionation has been investigated, and appropriate laser

406   parameters for the determination of S isotopes are presented below.

407

408   *3.4.1. Line scan versus spot ablation*

409   Experiments were carried out to examine the effect of single spot ('crater') versus line scan

410   ('raster') protocols on isotope fractionation and the precision obtainable by in situ analysis for

411   the anhydrite Sch-M-2 (Figure 6). Laser parameters, including laser optics and pulse energies

412   and frequencies, were kept the same for these comparisons. Line scan ablation results in higher

413   and non-decaying signal intensities, and is reflected in the long-term stability and greater

414   precision of S isotope ratios obtained by this protocol (Figure 6a). For spot mode analysis, signal

415   intensity deteriorates after approximately 90 seconds of ablation. Accordingly, the precision and

416   reproducibility of S isotope compositions using spot analysis diminishes significantly after

417   approximately the same length of time (Figure 6b). Degradation of signal intensity and analytical

418   precision is likely attributable to changes in crater geometry and increasing depth/radius aspect

419   ratio during ablation (Eggins et al., 1998; Horn et al., 2000; Russo et al., 2001). The causes of

420   signal reduction and isotope fractionation related to changes in crater geometry are not precisely

421   known, but may reflect decreasing laser irradiance and increasing thermal conductivity that

422   affect the efficiency of material volatilization and/or condensation, and particle transport at the

423   site of ablation (Eggins et al., 1998; Russo et al., 2001). In raster mode these effects can be

424   largely avoided because the trench depth and geometry remains relatively uniform during

425   ablation, and so differences in particle ablation and particle transport can be minimized. We note

426   that, within analytical uncertainty, Sch-M-2 is isotopically homogenous and does not explain the

427   large variability in isotope ratios measured during spot mode analysis (i.e., no heterogeneity is

428   sampled during depth profiling at a single spot).

429

430   Accordingly, line scan analysis is recommended for all in situ isotope measurements where

431   sufficient sample sizes and longer ablation times are available. The internal precision obtainable

432   by line scan mode is typically $\pm$ 0.25 ‰ (1σ). By comparison, the internal precision for spot

433   mode analysis is typically $\pm$ 0.5 – 0.6 ‰ (1σ) for samples ablated for periods of time up to

434   approximately two minutes. Spot mode analysis should be useful for rapid and approximate

435   determination of S isotopes when high precision ($\leq$ 1 ‰) is not required or sample size is

436   severely limited.

437

438   *3.4.2. Carrier gas composition and laser beam diameter*

439   The effect of varying carrier gas compositions to transport ablated material to the ICP has been

440   investigated extensively previously (Eggins et al., 1998; Günther and Heinrich, 1999b; Jackson

441   and Günther, 2003). Experimental data have indicated that the use of helium, as compared to

442   argon, for the carrier gas significantly increases signal intensities (two- to four-fold increase) and

443   reduces background (Eggins et al., 1998; Günther and Heinrich, 1999a). This observation has

444   been interpreted to reflect, (1) increased evaporation and decreased condensation of ablated

445   particles at the site of ablation and, (2) reduced sputtering of larger particles and increased

446   ionization efficiency of material in the ICP (Eggins et al., 1998; Günther and Heinrich, 1999b).

447   Incomplete vaporization and ionization of large particles in the ICP is a potential cause of

448   isotope fractionation (Jackson and Günther, 2003). Similar effects have been demonstrated for

449   elemental fractionation (Horn et al., 2000). The use of He as a carrier gas has been shown to

450   significantly reduce isotope fractionation (Jackson and Günther, 2003). Accordingly for our

451   study, helium is used as the carrier gas through the laser cell in all instances.

452

453   In addition, it has been demonstrated that particle size distribution is dependent on the diameter

454   of the incident beam (Figg et al., 1998; Jeong et al., 1999). Beam optic protocols to minimize the

455   formation of large particles should be adopted, in order to reduce potential isotope fractionation

456   associated with large particles (Jackson and Günther, 2003). The effect of varying beam diameter

457   on particle size distributions has not been examined explicitly because particle filtering apparatus

458   were not available for this study, but have been examined elsewhere (Guillong and Günther,

459   2002; Jackson and Günther, 2003). Large beam diameters and apertured beam optics will

460   distribute incident laser energy more evenly over the sample surface and may promote the

461   ablation of smaller, more uniformly-sized particles, which will be more efficiently ionized in the

462   ICP. Material ablated with large beam diameters exhibit significantly less mass discrimination

463   during isotope measurement (Horn et al., 2000), likely resulting from more quantitative and

464   equal ionization of all elements and/or isotopes. Similarly for our method, a large beam diameter

465   ~ 60 μm and defocused (apertured) beam optics are recommended for in situ S isotope

466   measurements because these should further minimize laser-induced isotope fractionation.

467

468 To validate these laser protocols, replicate sampling and analysis of the anhydrite mineral

469 standard Sch-M-2 was carried out by laser ablation MC-ICP-MS. Measured isotope

470 compositions were compared against data for the same standard analyzed using solution

471 techniques (Figure 7). The isotope composition of Sch-M-2 determined by in situ analysis is

472 $\delta^{34}S_{V-CDT} = 2.22 \pm 0.45$ ‰ (2σ, 12 replicates). This is identical, within analytical uncertainty, to

473 the isotope composition determined by bulk analysis; $\delta^{34}S_{V-CDT} = 2.12 \pm 0.26$ ‰ (2σ, 8

474 replicates). For both mineral and solution analyses, Sch-M-2 was bracketed by a matrix-matched

475 in-house solution standard (see section 3.4.3 for further details). These data indicate that the laser

476 parameters described previously introduce laser isotope fractionations that are within the

477 analytical uncertainties (~ 0.4 ‰) of our in situ S isotope method.

478

479 *3.4.3. Matrix-matching protocols*

480 The effects of matrix on isotope mass discrimination during in situ S isotope determination are

481 similar to those for bulk analysis. Because it is not possible to remove the complex matrix of

482 natural mineral samples for in situ analysis, it is necessary to assess and correct this matrix

483 fractionation using appropriately matrix-matched standards. Isotopically homogeneous,

484 calibrated and matrix-matched solid standards are not available for many natural mineral

485 samples. Therefore, it may be necessary to use matrix-matched solution standards to bracket

486 unknown mineral samples for in situ analysis. The matrix of solution standards can be readily

487 doped in order to match the wide range of matrix occurring in geologic samples. We have

488 investigated the validity of matrix-matching between solution standards and mineral samples.

489 Replicate analyses of the anhydrite standard Sch-M-2 using conventional solution methods and

490 matrix-matched (Ca-doped) bracketing standards yields an isotope composition $\delta^{34}S_{V-CDT} = 2.12$

491   ± 0.26 ‰. As presented in Figure 7, this is identical, within analytical uncertainty, to the isotope

492   composition determined by in situ analysis using identical matrix-matched solution standards;

493    $\delta^{34}S_{V-CDT} = 2.22 \pm 0.45$ ‰. These data are concordant with the S isotope composition obtained

494   previously for Sch-M-2 after chemical purification and analysis as a matrix-free sulfate solution

495   ($\delta^{34}S_{V-CDT} = 2.24 \pm 0.27$ ‰; Table 3). In contrast, significant and consistent deviations of

496   measured isotope ratios (up to 0.7 ‰) from 'true' isotope ratios are obtained when the Sch-M-2

497   standard is bracketed by non-matrix-matched standards. These data indicate that, although

498   instrumental mass bias introduced by the complex matrix of mineral samples cannot be removed

499   entirely, it can be appropriately corrected by bracketing with a standard of identical matrix. This

500   is important for obtaining the necessary 'accuracy' of S isotope compositions using this method.

501

502   **4. Application of bulk S-isotope analysis of sulfide and sulfate minerals**

503

504   *4.1. S isotope analysis of reference materials*

505   Because no internationally certified standard reference material is available for S-isotope

506   composition of pure sulfur (i.e. sulfate) solution, it is necessary to use in-house standard

507   solutions to bracket unknown sample solutions across multiple analytical sessions. The $\delta^{34}S$

508   isotope composition of our in-house standards, S_{Alfa} and S_{Spex}, have been calibrated against

509   reference material IAEA-S-1 and have been normalized to the V-CDT scale, assuming by

510   definition an isotope composition of IAEA-S-1 equal to $\delta^{34}S_{V-CDT} = -0.3$ ‰ (Coplen and

511   Krouse, 1998; Ding et al., 2001). Accordingly, the isotope compositions for our in-house

512   standards are $\delta^{34}S_{V-CDT}$ (Alfa) $= +1.91 \pm 0.21$ ‰ (2σ) and $\delta^{34}S_{V-CDT}$ (Spex) $= -2.99 \pm 0.18$ ‰

513   (2σ). The analysis of S isotope compositions of other RMs (IAEA-S-2, S-4 and NBS-123; Table

514   3) using our in-house analytes as bracketing standards are concordant with previously reported

515   values within analytical uncertainty (Taylor et al., 2000; Ding et al., 2001; Qi and Coplen, 2003).

516   These data confirm the consistency of our S isotope measurements and the validity of standard-

517   sample bracketing. Reproducibility is typically 0.2 ‰ and is consistent across a wide range of

518   sample material and S-isotope compositions. For example, determination of the S-isotope

519   composition of purified seawater sulfate from Woods Hole, MA (in-house seawater standard)

520   yields a value of $\delta^{34}S_{V-CDT} = 21.22 \pm 0.19$ ‰ (2σ), which is undistinguishable within error from

521   the consensus value for modern seawater (Rees et al., 1978). Analysis of S-isotope compositions

522   of both sulfate- and sulfide-bearing reference minerals yielded similar results.The S-isotope

523   compositions determined for the purified in-house standards Sch-M-2 (evaporate anhydrite) and

524   GAV-18 (hydrothermal pyrite) are $\delta^{34}S_{V-CDT} = 2.27 \pm 0.12$ ‰ and 9.66 ± 0.2 ‰, respectively.

525   These isotopic values are within analytical error of S-isotope compositions determined

526   previously using conventional techniques (Table 3).

527

528   *4.1.S isotope analysis of hydrothermal and sedimentary sulfides*

529   We have analyzed a selection of natural sulfides from sedimentary and hydrothermal

530   environments (Table 4). Sulfur isotope studies provide valuable information for determining

531   sulfur sources and precipitation mechanisms in submarine hydrothermal deposits. Several

532   mechanisms have been proposed to explain variations in the $\delta^{34}S$ values of sulfides in seafloor

533   hydrothermal systems (Janecky and Shanks, 1988; Herzig et al., 1998; Shanks, 2001) and

534   indicate that sulfur has three major sources: (1) sulfur from the leaching of igneous rocks, (2)

535   sulfur from the reduction of a small amount of admixed seawater-derived sulfate, and (3) sulfur

536   produced by disproportionation of magmatic SO_2 in back-arc hydrothermal systems. Sulfur

537   isotope results from modern hydrothermal pyrite and chalcopyrite (Table 4) are consistent with

538   previously reported studies (Herzig et al., 1998; Bach et al., 2003; Rouxel et al., 2004). We

539   observe an overall range of $\delta^{34}S$ values between -3.4 to $+6.3$ ‰ suggesting that this technique

540   can be used to infer S geochemical cycling in seafloor hydrothermal systems, such as seawater

541   sulfate reduction (increasing S isotope composition) and magmatic S input (producing negative

542   S-isotope composition). In some cases, the difference from published values is significant (up to

543   0.6 ‰) but may result from sample heterogeneity not identified by bulk analysis.

544

545   We have also analyzed a selection of natural sulfides from sedimentary environments (Table 4).

546   Pyrite formation in modern organic-rich marine sediments is mediated by sulfate-reducing

547   bacteria and proceeds through the dissolution and reduction of lithogenic Fe-oxides and silicates

548   to Fe(II), either below the sediment-water interface during diagenesis or in the stratified euxinic

549   bottom waters syngenetically (Canfield, 1989; Anderson and Raiswell, 2004). Hence, S isotope

550   composition of sedimentary pyrite can provide valuable information to distinguish between

551   diagenetic and syngenetic pyrite formation as well as sulfur geochemical cycling in ancient

552   oceans (Zaback et al., 1993; Calvert et al., 1996; Lyons, 1997; Werne et al., 2003; Neretin et al.,

553   2004). Sulfur isotope compositions of pyrite from black shales are also reported in Table 4 and

554   display an overall range of 55 ‰. Small fractionation of S isotopes in late Archean sedimentary

555   sulfides (Jeerinah Formation; Table 4) is consistent with previous studies suggesting sulfate

556   reduction at low sulfate concentrations (Canfield et al., 2000) due to low levels of atmospheric

557   oxygen (Farquhar et al., 2000; Ono et al., 2003). The significant increase in the S isotope

558   fractionation in sedimentary pyrite at 2.32 Ga has been interpreted as reflecting an increase of

559   seawater sulfate concentrations in the aftermath of the rise of atmospheric oxygen (Cameron,

560   1982; Canfield, 1998; Bekker et al., 2004; Kah et al., 2004). Because this technique is

561   compatible with other non-traditional stable isotope techniques, such as those used for Fe-isotope

562   determination in sedimentary sulfides (Rouxel et al., 2005), it is possible to apply coupled S and

563   Fe stable isotope approaches for the study of ancient S- and Fe- biogeochemical cycling.

564

565   **5. Application of in-situ S isotope analysis of sulfide and sulfate minerals**

566

567   *5.1. Assessment of mass fractionation and external reproducibility*

568   Our instrumental setup for in situ analysis requires no modification to the physical configuration

569   or operating parameters used for bulk solution analysis. Bulk and in situ measurements can be

570   performed interchangeably within a single analytical session. We use the standard-sample

571   bracketing technique for the isotope determination of unknown mineral samples, identical to

572   bulk S isotope measurements. We recognize and caution that the mechanics of particle ablation,

573   aerosol transport and ionization in the ICP are significantly more complex than for solution

574   aspiration. This may result in isotope mass fractionation and accordingly poor analytical

575   precision or inaccurate data. We have presented laser protocols that minimize mass bias

576   introduced by the laser, and which are concordant with results of previous studies (Outridge et

577   al., 1997; Eggins et al., 1998; Figg et al., 1998; Günther and Heinrich, 1999b; Jeong et al., 1999;

578   Horn et al., 2000; Russo et al., 2001; Guillong and Günther, 2002; Jackson and Günther, 2003).

579   Further, differences in the behavior of aerosols for ablated particles as compared to aspirated

580   solutions will contribute to the overall uncertainty of in situ isotope measurement using standard-

581   sample bracketing. Despite these potential difficulties, replicate analysis of the mineral standards

582   indicates relatively precise and consistent isotope ratio determinations as compared to isotope

583   compositions determined by independent bulk analyses (Table 5). The long-term reproducibility

584   of our in situ technique is approximately $\pm$ 0.45 ‰ (2σ). Further, the isotope composition of Sch-

585   M-2 determined by bulk ($\delta^{34}S_{V\text{-}CDT}$ = 2.12 $\pm$ 0.26 ‰) and in situ ($\delta^{34}S_{V\text{-}CDT}$ = 2.22 $\pm$ 0.45 ‰)

586   techniques are identical within these analytical uncertainties, indicating no consistent bias of

587   offset from mass bias corrections using standard-sample bracketing with appropriately matrix-

588   matched standards. This should enable S isotope determinations for a wide range of natural

589   sulfur-bearing samples for which well-characterized, isotopically-homogeneous and

590   appropriately matrix-matched solid standards do not exist.

591

592   *5.2. Future applications of in situ S-isotope analysis of sulfide and sulfate minerals*

593   Determination of S isotopes using laser-ablation MC-ICP-MS may provide additional

594   information about geochemical and biological processes that might not otherwise be obtained

595   using bulk techniques. A primary application of our in situ analytical routine is to examine S

596   isotope variability in sulfur-bearing hydrothermal and sedimentary materials relevant to the study

597   of sulfide-sulfate deposition in modern and ancient marine environments. In situ analysis is

598   particularly important for systems where significant variations in S isotope compositions may be

599   recorded on small (μm to cm) spatial scales (e.g., within hydrothermal sulfide-sulfate veins or

600   sulfide chimney deposits). In addition, in situ analyses may be necessary for samples for which it

601   is difficult to chemically or physically eliminate matrix from the analyte (e.g., co-existing

602   sulfides or sulfide-sulfate minerals). We have applied our in situ method to the determination of

603   S isotopes in a suite of hydrothermal and sedimentary sulfides and sulfates and can compare our

604   data versus isotope compositions determined using conventional techniques. Overall, the data are

605   in excellent agreement for the range of sulfide and sulfate minerals examined (Table 5). For

606   samples that appear to be isotopically homogeneous based on replicate in situ analyses, our data

607   are the same, within analytical error, to S isotope compositions determined by independent

608   methods. We identify no consistent or significant deviation between S isotope ratios determined

609   by laser ablation MC-ICP-MS and other techniques, which would otherwise indicate some

610   unaccounted mass fractionation by our method. For several sulfide and sulfate, we identify

611   significant isotopic heterogeneity within single samples on spatial scales of mm. These variations

612   are not likely due to matrix artifacts, because in all cases unknown samples are calibrated against

613   matrix-matched standards. Rather, the data likely demonstrate real geochemical heterogeneity

614   recorded by the sample. It is beyond the scope of this paper to discuss the origin of the S isotope

615   variations observed, however our data demonstrate that in situ analytical approaches to S isotope

616   determination can provide information about geochemical processes that might otherwise be

617   overlooked by bulk, conventional techniques.

618

619   **6. Conclusions**

620

621   We have developed a technique for the rapid, precise and consistent determination of S isotopes

622   (δ^{34}S) by bulk and in situ MC-ICP-MS applicable for a range of sulfur-bearing materials. Major

623   isobaric interferences from molecular $^{16,17,18}O_2^+$ on sulfur masses of interest are removed by

624   applying sufficient mass resolution and determining sulfur intensities on interference free

625   plateaus. Hydride (^{32}S-^{1}H, ^{33}S-^{1}H) and argon (^{36}Ar) interferences are not fully resolved with high

626   mass resolution and limit the application of MC-ICP-MS techniques for accurate multiple S

627   isotope (δ^{33}S, δ^{36}S) determination. We have examined potential contributions to background

628   sulfur signal, including blank contamination and unresolved spectral interferences (e.g., O_2-

629   tailing due to mass drift). Background intensities on sulfur are typically small (30 – 50 mV on

630   ^{32}S), but may be variable over the course of an analytical session. Average background

631   intensities are determined for each isotope (on-peak zero) and are directly subtracted from the

632   signal intensity for each sulfur isotope as part of off-line evaluation. Approaches to minimize the

633   magnitude of the background correction required to within limits of analytical precision are

634   advantageous because the concentration and isotopic composition of the blank are inherently

635   variable and difficult to characterize. Accordingly, the following procedures are recommended;

636   (1) measure isotope ratios of standard and sample analytes at minimum signal intensities ~ 10

637   volts and, (2) determine isotope compositions of unknown samples with a standard analyzed at

638   the same intensity (within ~ 20 %). By closely matching signal intensities, the mass bias

639   accounting for effects of instrumental fractionation and background as calculated for the

640   standard, can be appropriately applied to unknown samples.

641

642   Instrumental mass bias is corrected by applying the standard-sample bracketing technique,

643   whereby the mass bias calculated for two standard runs immediately before and after are applied

644   by linear interpolation to the unknown sample. We have presented a rigorous examination of

645   matrix effects for S isotope determination by MC-ICP-MS and show that matrix artifacts can

646   produce variable and significant mass bias (up to 0.7 ‰). It is essential that S isotope ratios of

647   samples be determined using appropriately matrix-matched standards. For bulk S isotope

648   analysis, we have described a chemical purification method that is applicable for a wide range of

649   sulfide and sulfate materials whereby the matrix is removed. For in situ analysis, where the

650   matrix cannot be removed prior to analysis, it is essential that appropriately matrix-matched

651   standards be used to correct instrumental mass bias. An important development of our standard-

652   sample bracketing methods is the ability to determine accurate and precise S isotope

653   compositions in *aqueous and mineral samples* with a wide range of matrix, using matrix-

654   matched solution standards in both cases. This has particular application for the in situ analysis

655   of many sulfur-bearing minerals for which certified solid standards with correct matrix do not

656   exist. We have examined sources of isotope fractionation introduced by the laser process. In

657   order to apply the standard-sample bracketing method appropriately using solution standards, it

658   is necessary to minimize laser-induced mass bias to within acceptance limits of uncertainty for

659   the method. Recommended laser protocols are discussed that should enable precise and

660   consistent S isotope ratio measurement by laser ablation MC-ICP-MS.

661

662   We have validated the robustness of our analytical method by multiple determinations of

663   reference materials. S isotope ratios for reference materials determined by this study and by

664   independent techniques show excellent agreement demonstrating the 'accuracy' of our method.

665   For solution analysis, the long-term reproducibility of S isotope measurements is typically $\pm$ 0.20

666   ‰ (2σ). For in situ analyis, the external precision calculated by replicate measurement of

667   homogeneous mineral standards is $\pm$ 0.45 ‰ (2σ). Importantly, there is good agreement between

668   S isotope ratios for the same standards determined by bulk and in situ analysis (within 0.2 ‰),

669   indicating that standard-sample bracketing can appropriately correct for instrumental mass bias

670   and that laser-induced mass bias is smaller than analytical uncertainties. In addition, we have

671   performed preliminary S isotope determination for a range of natural sulfide and sulfate minerals

672   by laser ablation MC-ICP-MS. Again, the results of this study demonstrate excellent agreement

673   with published data. The analytical technique presented here should enable precise and accurate

674 S isotope measurement for a wide range of sulfur-bearing materials – in particular for geologic

675 samples with complex matrix for which high-precision, high-resolution in situ analysis is critical.

676

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678

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Figure Captions

Figure 1.

Schematic diagram of the introduction system to the NEPTUNE MC-ICP-MS. Standard and sample solutions are taken up in Ar gas flow and introduced as a 'wet' aerosol (in 2% HNO_3) into the ICP torch via a cyclonic spray dual chamber. During in situ analysis, ablated material is carried via He gas flow into the cyclonic spray dual chamber where it is mixed with ultra-pure 2% HNO_3 to yield a wet aerosol.

Figure 2.

Peak shapes for S-isotopes at masses 32 (diamond), 33 (square) and 34 (triangle) for aspiration of a 20 ppm S solution. Beams are collected simultaneously on three individual Faraday Cups in 'high-resolution' mode. Significant interferences from O_2^+ occur on all sulfur masses (light-gray bar) and must be removed using sufficient mass resolution to enable detection of S-isotopes on the interference-free plateau at lower mass (dark-gray bar).

Figure 3.

Variability of measured $^{34}S/^{32}S$ isotope ratio as a function of ^{32}S signal intensity for S_{Alfa} standard solution. For signal intensities below 1 volt (equivalent to ~ 2 ppm S) mass bias toward heavy $^{34}S/^{32}S$ ratios is significant resulting from blank artifacts (highlighted gray area) that require appropriate correction.

Figure 4.

Long-term reproducibility of S-isotope for in-house solution standards S_{Alfa} and S_{Spex} calibrated against certified standards over multiple, independent analytical sessions. Data are shown relative to the in-house S_{Spex} scale. For $\delta^{34}S$ values, the reproducibility is within $\pm$ 0.2 ‰ for both solutions. For $\delta^{33}S$, the reproducibility is poor because of variable and significant interference on mass 33 from formation of ^{32}S-^{1}H hydride.

Figure 5.

Assessment of matrix effects on measured S-isotope ratios for a range of elements with stoichiometry appropriate to various sulfide and sulfate minerals (shown with open circles). Element-doped S solutions are measured and isotopic compositions are expressed as permil deviation on the V-CDT scale from the composition determined for the pure S (i.e., sulfate) standard ($\Delta^{34}S = \delta^{34}S_{(matrix\ solution)} - \delta^{34}S_{(pure\ S\ solution)}$). The element-doped solutions were purified and the isotope composition re-determined (filled diamonds). Following purification, the deviation between the pure S standard and purified solutions is within analytical uncertainty. External precision calculated at $\pm$ 0.2 ‰ is shown by the gray bar.

Figure 6.

Signal intensities and measured isotope ratios for anhydrite standard Sch-M-2 using (a) line scan ('raster') ablation and (b) single spot ablation. ICP-MS operating parameters were identical for acquisition of both data. Signal intensities for line scan ablation are significantly higher as compared to spot ablation and remain high throughout the ablation period. Accordingly, $^{34}S/^{32}S$ isotope ratios determined for line scan analysis are more precise and consistent with isotope ratios for Sch-M-2 determined using conventional bulk techniques (shown by horizontal gray

bar; $\delta^{34}S = 2.27 \pm 0.24$ ‰, 2σ). The oscillating fluctuation of signal intensity for line scan mode arises because the mass of material ablated material varies as extra laser pulses are applied to a single area during changes of the direction of sample movement in line scan analysis. This artifact does not compromise the precision obtainable by in situ analysis at these high signal intensities.

Figure 7.

Comparison of S isotope compositions determined for the in-house anhydrite standard Sch-M-2 using *bulk* analysis (gray diamonds) and in situ analysis (gray circles). In both cases, the isotope value composition of anhydrite was calibrated against a matrix-matched (Ca-doped) sulfur standard, S_{Alfa}. The isotopic compositions determined for Sch-M-2 are identical within analytical uncertainties for both methods using matrix-matching procedures. Significant mass bias offset is observed for Sch-M-2 when calibrated against a non-matrix-matched S_{Alfa} standard, resulting in erroneous S isotope determinations (white diamonds). Error bars for single analyses are 1σ (internal precision). Mean isotope compositions calculated from replicate analyses are reported at 2σ (external precision).

Table 1 Typical operating parameters for NEPTUNE MC-ICPMS and NewWave UP213 laser.

Mass Spectrometer Setup

MC-ICP-MS	ThermoElectron NEPTUNE
RF power	~ 1150 W
Pt-guard electrode	On, grounded
Gas flows	
Cooling gas	~ 15 L/min, Ar
Auxiliary gas	~ 0.8 L/min, Ar
Sample gas	~ 0.8 - 0.9 L/min, Ar
Laser "carrier" gas	~ 0.35 - 0.4 L/min, He
Interface cones	X-cones (Ni)
Analyzer pressure	~ 10^{-9} torr
Nebulizer	PFA-50, Elemental Scientific, Inc.
Sample uptake rate	50 μL/min
Spray Chamber	SSI cyclonic spray dual chamber, Elemental Scientific, Inc.

Data Acquisition Parameters

Acquisition mode	Static, analogue detectors
Detection system	Faraday cups
Cup configuration	^{32}S (L3), ^{33}S (C), ^{34}S (H3)
Resolution mode	High (entrance slit); Low (detector slit)
Signal analysis protocol	8.5 sec integration per cycle, 20 cycles.
Wash-out time	2 min (solution); 4 min (laser)

Laser Setup

Laser	New Wave UP213, (quad Nd:YAG 213 nm laser)
Carrier gas	Helium
Beam optics	Apertured Mode
Spot diameter	60 μm
Raster protocols	Pattern area 180 x 80 μm, Line spacing 15 μm
Scan speed	5 μm/s
Ablation duration (analysis time)	260 s
Pulse rate	10 Hz
Laser intensity	50 - 70 % (~ 0.4 mJ)
Energy density	~ 9 - 10 J/cm^2
Pre-ablation	same raster and spot size, scan speed 30 μm/s, intensity 40 %

Table 2 Isobaric (spectral) interferences on sulfur isotope masses

Isotope	Abundance (%)	Interference	Abundance	m/Δm
^{32}S	94.93	^{16}O-^{16}O	99.52	1801
		$^{64}Zn^{2+}$	48.89	-4562
		^{15}N-^{16}O-^{1}H	0.37	1040
^{33}S	0.76	^{17}O-^{16}O	0.08	1461
		^{16}O-^{16}O-^{1}H	99.51	1260
		^{32}S-^{1}H	95.01	3907
		$^{66}Zn^{2+}$	27.81	-3905
^{34}S	4.29	^{18}O-^{16}O	0.4	1297
		^{17}O-^{16}O-^{1}H	0.76	1000
		^{33}S-^{1}H	0.75	2977
		$^{68}Zn^{2+}$	18.56	-6238
^{36}S	0.02	^{36}Ar	0.34	77083
		^{35}Cl-^{1}H	75.76	3747

Table 3 Reference materials and standards determined by this study

Name	Sample Type	# of replicates	$\delta^{34}S$ Spex	$2\sigma^{\$}$	$\delta^{34}S$ VCDT	$2\sigma^{\xi}$	$\delta^{34}S$ VCDT *
Reference Materials							
IAEA-S-1	Synthetic Ag_2S	13	2.69	0.21	-0.30	0.28	-0.30 (a,b)
IAEA-S-2	Synthetic Ag_2S	11	25.43	0.39	22.44	0.43	22.67 ± 0.26 (c)
IAEA-S-4	Elemental S	10	19.54	0.22	16.55	0.29	16.9 ± 0.2 (e)
NBS-123	Natural ZnS	11	20.76	0.19	17.77	0.26	17.44 ± 0.2 (c,d)
In-house Standards							
Alfa	Specpure SO_4^{2-} solution	20	4.90	0.24	1.91	0.30	n.d.
Sch-M-2	Permian Anhydrite, $CaSO_4$	8	5.23	0.20	2.24	0.27	2.49 ± 0.2
SW-Woods Hole	Modern Seawater, Woods Hole	4	24.18	0.19	21.19	0.27	20.99 (f)
FeIII-sulfate	Synthetic $Fe_2SO_4.3H_2O$	6	11.33	0.14	8.34	0.23	n.d.
GAV-18	Hydrothermal pyrite, FeS_2	8	12.61	0.19	9.62	0.27	9.70
Ward's Py	Hydrothermal pyrite, FeS_2	7	5.56	0.28	2.57	0.33	n.d.
Ward's Po	Hydrothermal pyrrhotite, FeS	3	3.67	0.17	0.68	0.25	n.d.

$^{\$}$ External precision (two standard deviations) calculated from replicate analyses

$^{\xi}$ External precision calculated (two standard deviations) using error propagation of uncertainties of sample and bracketing standard. i.e., $2\sigma = \sqrt{((2\sigma \text{ of sample})^2 + (2\sigma \text{ of Spex standard})^2)}$

* published data, errors given at 2σ uncertainty: (a) Coplen and Krouse, 1998; (b) Ding et al., 2001; (c) Taylor et al., 2000; (d) Hut, 1987; (e) Qi and Coplen, 2003; (f) Rees et al., 1978

Table 4 Bulk analysis of representative natural sulfides from hydrothermal and sedimentary environments

Name	Sample Type	δ^{34}S Spex	$1\sigma^{\$}$	δ^{34}S VCDT	$1\sigma^{\$}$	δ^{34}S VCDT *
Modern Hydrothermal Sulfides						
MS-18-05 cpy	chalcopyrite	**8.32**	0.11	**5.33**	0.21	**5.0 (a)**
MS-21-03 cpy	chalcopyrite	**9.32**	0.13	**6.33**	0.22	**5.6 (a)**
NL-16-02 cpy	chalcopyrite	**-0.36**	0.11	**-3.35**	0.21	**-3.4 (b)**
83-504B-80R1,62	pyrite	**6.57**	0.27	**3.58**	0.32	**3.5 (c)**
83-504B-84R2,34	pyrite	**6.75**	0.27	**3.76**	0.32	**4.0 (c)**
Kentucky Black Shales, Clay City (Devonian)						
Clay City. 510-519 #2	pyrite	**-16.81**	0.49	**-19.80**	0.52	**(d)**
ClayCity, 193-200 Leach	pyrite	**-18.53**	0.09	**-21.52**	0.20	
ClayCity, 232-238 Leach)	pyrite	**-21.18**	0.08	**-24.17**	0.20	
Black Shales, Illinois Basin (Devonian)						
SH-Dev-1 #1	pyrite	**26.17**	0.19	**23.18**	0.26	**(d)**
SH-Dev-2 #1	pyrite	**-0.68**	0.20	**-3.67**	0.27	
SH-Dev-3 #1	pyrite	**-7.99**	0.14	**-10.98**	0.23	
SH-Dev-3 #2	pyrite	**-8.28**	0.16	**-11.27**	0.24	
SH-Dev-3 #3	pyrite	**-7.63**	0.23	**-10.62**	0.30	
2.32 Ga Rooihoogte and Timeball Hill Formations, Transvaal Basin, South Africa						
EBA-2/55	pyrite	-25.17	0.07	-28.16	0.19	-29.1; -29.6 (e)
EBA-2/59	pyrite	-23.96	0.08	-26.95	0.20	-25.6; -28.8 (e)
EBA-2/60	pyrite	-28.97	0.00	-31.96	0.18	-28.9; -30.0 (e)
EBA-2/67	pyrite	-25.67	0.27	-28.66	0.32	-23.9; -29.9 (e)
2.63 Ga Royal Hill Member of the Jeerinah Formation, Hamersley Basin, Western Australia						
FVG-1, 722.6	pyrite	**6.10**	0.10	**3.11**	0.21	**-0.4 to 6.3 (f)**
FVG-1, 752.8	pyrite	**5.85**	0.11	**2.86**	0.21	
FVG-1, 761.8	pyrite	**7.92**	0.00	**4.93**	0.18	
FVG-1, 787.4	pyrite	**5.53**	0.04	**2.54**	0.18	
FVG-1, 849.6	pyrite	**1.07**	0.04	**-1.92**	0.18	

[$] Internal precision (one standard deviation) for individual measurement.

[*] Published data (a) Rouxel et al., 2004; (b) Herzig et al., 1998; (c) Bach et al., 2003; (d) A. Bekker, *pers. comm.* (e) Bekker et al., 2004; (f) Ono et al., 2003

Table 5 In situ sulfur isotope analysis of natural sulfides and sulfates from hydrothermal and sedimentary environments

Name	Sample Type	δ^{34}S Spex	δ^{34}S VCDT[ξ]	δ^{34}S VCDT[$]
Hydrothermal Sulfides				
ALV-4053-M1 #A1	marcasite			**2.0 ± 0.2 (a)**
raster #1		**5.21**	**2.21**	
raster #2		**5.31**	**2.31**	
raster #3		**5.14**	**2.14**	
GAV-18	pyrite			**9.7 ± 0.2 (b)**
raster #1		**12.83**	**9.84**	
raster #2		**12.93**	**9.94**	
raster #3		**13.38**	**10.39**	
FL-19-9	pyrite			**0 ± 0.2 (c)**
raster #1		**2.77**	**-0.22**	
raster #2		**3.35**	**0.36**	
raster #3		**3.54**	**0.55**	
raster #4		**3.51**	**0.52**	
2.32 Ga Rooihoogte and Timeball Hill formations, Transvaal Basin, South Africa				
EBA-2/30	pyrite			**-25.6; -26.2 (d)**
raster #1		**-26.21**	**-29.21**	
raster #2		**-25.83**	**-28.83**	
raster #3		**-25.49**	**-28.49**	
raster #4		**-25.62**	**-28.62**	
raster #5		**-24.85**	**-27.85**	
raster #6		**-25.40**	**-28.40**	
raster #7		**-24.95**	**-27.95**	
raster #8		**-19.87**	**-22.87**	
raster #9		**-19.47**	**-22.47**	
raster #10		**-20.46**	**-23.46**	
raster #11		**-21.83**	**-24.83**	
Hydrothermal Sulfates				
193-1188A-7R-1	anhydrite			**21.6 (e)**
raster #1			**21.22**	
raster #2			**21.22**	
raster #3			**21.13**	
raster #4			**21.07**	
193-1188F-26Z-1	anhydrite			**18.3 (e)**
raster #1			**16.61**	
raster #2			**17.43**	
raster #3			**18.55**	
raster #4			**18.00**	
raster #5			**19.01**	
raster #6			**18.65**	

[ξ] Normalized to V-CDT scale using δ^{34}S of in-house Spex vs. V-CDT = - 2.99 ‰

[$] Determined using conventional, bulk analysis; (a) Rouxel et al., 2007; (b) Rouxel, *unpubl.,* this study; (c) Rouxel et al., 2004; (d) Bekker et al., 2004; (e) Bach et al., 2005

He gas

Laser cell

Sample (solid)

Cyclonic spray chamber

Aerosol

NEPTUNE MC-ICPMS

ICP torch

Ar gas

Sample/ Standard (solution in 2% HNO₃)

PFA-nebulizer

Pump

Waste

Top panel: $\delta^{34}S_{(Spex)}$ versus Number of Replicates. *Alfa* $\delta^{34}S = 4.91 \pm 0.21$. *Spex* $\delta^{34}S = 0.00 \pm 0.18$.

Bottom panel: $\delta^{33}S_{(Spex)}$ versus Number of Replicates. *Alfa* $\delta^{33}S = 2.3 \pm 2.9$. *Spex* $\delta^{33}S = 0.0 \pm 2.1$.