Off-mount calibration and one new potential pyrrhotite reference material for SIMS sulfur isotope analysis

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13   **Abstract**

14   Sulfur isotope analysis of three sulfide (two pyrite and one pyrrhotite samples) on two epoxy mounts

15   shows that the mount to mount variation of raw $\delta^{34}S$ value is negligible when SIMS analytical settings

16   remain stable, and thus an off-mount calibration procedure for SIMS sulfur isotope analysis is applied in

17   this study.

18   YP136 is a pyrrhotite sample collected from northern Finland. Examination of thin section under

19   polarizing microscope, BSE image analyses and WDS mapping show that the sample grains display no

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20   internal growth or other zoning. Total 318 spot multiple sulfur isotope analyses conducted on more than

21   100 randomly selected grains yielded highly consistent sulfur isotopic ratios. The reproducibility of all

22   the analytical results of $^{34}S/^{32}S$ is 0.3‰ (2s, n=318), which is same with that of the well characterized

23   pyrite reference materials PPP-1 and UWPy-1. Its $\delta^{34}S$ values determined by gas mass spectrometry is

24   1.5 ± 0.1‰ (2s, n=11), which agrees with the SIMS data (1.5 ± 0.3‰, 2s) calibrated by another pyrrhotite

25   standard Po-10. Therefore, YP136 pyrrhotite is a candidate reference material for micro *in-situ* sulfur

26   isotope analysis.

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28   **Keywords**: Off-mount calibration; SIMS; Pyrrhotite; Reference material; Sulfur isotope

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30   **1. INTRODUCTION**

31   Sulfides are commonly present in many kinds of rocks and deposits, and their sulfur isotope

32   composition can help to constrain the sulfur source and ore-forming processes (Rye and Ohmoto, 1974,

33   Huston *et al.* 1995, Large *et al.* 2009, Scott *et al.* 2009, Wagner *et al.* 2010, Ulrich *et al.* 2011). However,

34   using traditional bulk sulfur isotope analysis, it is difficult to avoid contaminations from mineral

35   inclusions, crack impurities or adhesive neighboring minerals when replacement texture occurs (Chen *et*

36   *al.* 2010). Moreover, sulfides generally have a multi-stage growth history and significant isotopic

37   variation even within single grain (Chen *et al.* 2015, Williford *et al.* 2011, Zhang *et al.* 2017). Therefore,

38   *in-situ* sulfur isotope analysis is necessary for sulfur isotope studies. Given its high sensitivity and high

39   spatial resolution, secondary ion mass spectrometry (SIMS) has been widely used for *in-situ* sulfur

40   isotope analysis in recent years. Instrumental mass fractionation (IMF) is a major problem during SIMS

41   analysis (Hartley *et al.* 2012) and the most important contributor of IMF during SIMS analysis is

42 ionization process, which depends on chemical composition of samples (Valley and Kita 2009, Othmane

43 *et al.* 2015). The IMF can be corrected by using mineral standards that have similar chemical composition

44 to the unknown sample (Othmane *et al.* 2015). Although previous studies do not mention how they

45 mounted standards, co-mount standards were generally applied. However, segment mounted standards

46 co-mounted in the same holder for sulfur isotope (Whitehouse, 2013) and off-mounts standards for

47 oxygen and magnesium isotope analyses (Kita *et al.* 2009, MacPherson *et al.* 2010) have been introduced.

48 In this study we present results from 6 days SIMS sulfur analysis, which demonstrate that off-mount

49 calibration is also feasible for SIMS sulfur isotope measurement. Using this method, we obtained 318

50 spot sulfur isotope analyses for a pyrrhotite sample (YP136) conducted on more than 100 randomly

51 selected grains in 22 separated sample mounts. Our results show that this sample is a candidate reference

52 material for micro *in-situ* sulfur isotope determination. The sample is also characterized by gas mass

53 spectrometer, BSE image analyses and WDS mapping. This pyrrhotite sample is available in large

54 enough quantities to be shared by LA-ICP-MS or SIMS laboratories worldwide for comparison purposes.

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56 **2. SAMPLE DESCRIPTION AND PREPARATION**

57 Two natural pyrite reference materials (RM), PPP-1 (Gilbert *et al.* 2014) and UWPy-1 (Crowe and

58 Vaughan, 1996; Ushikubo *et al.* 2014), one pyrrhotite Po-10 (Gilbert *et al.* 2014) and a natural pyrrhotite

59 sample YP136 from the Portimo mafic complex were used in this study. The 2.44 Ga Portimo mafic

60 complex is located northern Finland and belongs to the Tornio-Näarankavaara belt running from the

61 western to eastern border of Finland (Fig. 1 in Iljina and Hanski 2005). It was emplaced into Archean

62 basement granitoids and has been dismembered to four blocks during Svecofennian orogeny (Iljina and

63 Hanski 2005). Each individual block contains a basal marginal series of variable thickness from tens of

3

64 meters to more than one hundred meters, and an overlying layered series of hundreds of meters. Different

65 type of PGE mineralization mainly in disseminated sulfide occur in this complex including reef-type in

66 the internal part of the layered sereis, marginal-type near the basal contact, and offset type in the basement,

67 with approximately 46.8 Mt PGE-Ni-Cu resources (Iljina *et al.* 2015). Except for PGE mineralization,

68 discontinuous massive sulfide layer with thickness varying from 20 cm to 20 m occur in the marginal

69 series either below or above the basal contact. The YP136 pyrrhotite sample (Fig. 1a) was collected from

70 a drill core (YP136) which penetrates a massive sulfide layer near the marginal zone in the Suhanko

71 block of the Portimo complex (Iljina and Hanski 2005). It is massive and dark-brown (Fig. 1a), fine

72 grained (Fig. 1b) under polarizing microscope. Pyrrhotite consist 99% of this sample, with minor

73 pentlandite exsolution, which is similar with another homogeneous pyrrhotite sample (Alexo pyrrhotite)

74 collected from the 2.70 Ga Alexo Ni-Cu-(PGE) deposit in Canada (LaFlamme *et al.* 2016). Both BSE

75 images (Fig. 1c) and WDS mapping (Figs. 1d-e) of this sample show no internal growth or other zoning.

76   The samples were crushed and affixed onto double faced adhesive tape on a flat sheet glass. The

77 samples were then cast into epoxy. All the samples were mounted in the middle 8 mm (in radius) of the

78 mount. Randomly selected grains of sample PPP-1, Po-10, and YP136 were put in two mounts (mount 1

79 and 2), while UWPy-1 pyrite was also mounted into mount 1. The standard samples, on mount 1 are used

80 to monitor IMF. Sample YP136 on mount 1 and all the samples including standards and YP136 on mount

81 2 are treated as unknown samples to evaluate the mount to mount fractionation. To monitor long term

82 drift of the IMF and evaluate its homogeneity and test the reliability of analytical procedure, more than

83 200 grains of sample YP136 were also mounted and analyzed on other 20 mounts with other unknown

84 samples beyond the scope of this study. All the epoxy mounts were carefully polished several times with

85 diamond paste grain size reducing gradually. All the mounts were first washed in ethanol, and deionized

86 water, then put into the oven and baked for 3 hours at temperature 40℃. Before SIMS analysis, sample

87 mounts were coated by a gold layer with a thickness of about 30 nm.

88

89 **3. MEASUREMENT METHODS**

90 **3.1. SIMS**

91   The SIMS analysis was conducted at the Guangzhou Institute of Geochemistry, Chinese Academy

92 of Sciences (GIGCAS) using a CAMECA IMS 1280-HR. Analytical parameters were kept the same

93 during the whole session and were summarized as follows: A primary $^{133}Cs^+$ ion beam (~2.0 nA current

94 and 20 keV total impact energy) was focused on the sample surface with a spot diameter of 10 μm. A 15

95 μm raster was applied during all analyses to slightly homogenize the Gaussian beam. 20 s pre-sputtering

96 was applied to remove the Au coating, and a normal-incidence electron gun was used for charge

97 compensation. The mass resolving power was set at ~5000 to avoid isobaric interferences. NMR field

98 sensor was applied to stabilize the magnetic field. ^{32}S, ^{33}S and ^{34}S were measured simultaneously by three

99 Faraday cups of the multi-collection system (L'2, L1 and H1 respectively). The amplifier gains were

100 automatically calibrated before start of the whole session. Total analysis time for one spot is about 4.5

101 minutes.

102   Correction factors of instrument bias of $\delta^{34}S$ were determined by $\delta^{34}S_{raw}$ values of analyses of

103 standards as follows:

104      $\alpha_{(SIMS)} = (^iS/^{32}S)_{standard\ raw}/(^iS/^{32}S)_{standard\ recommend}$

105   Values of $(^iS/^{32}S)$ of unknown samples were calculated as follows:

106      $(^iS/^{32}S)_{sample} = (^iS/^{32}S)_{measured}/\alpha_{(SIMS)}$

107   where i = 33, 34

108   Corrected ratios of $^{34}S/^{32}S$ and $^{33}S/^{32}S$ were normalized to the Vienna Canyon Diablo Troilite (V-

109   CDT) value ($^{34}S/^{32}S$ = 1/22.6436, $^{33}S/^{32}S$ = 1/126.948, Ding *et al.* 2001), according to the following

110   equations and taken as "raw" δ-value ($\delta^{i}S_{raw}$).

111        $\delta^{i}S_{sample} = [(^{i}S/^{32}S)_{sample} / (^{i}S/^{32}S)_{V\text{-}CDT} - 1] \times 1000$

112   Typical $\delta^{i}S_{raw}$, α and $\delta^{i}S$ values of UWPy-1, PPP-1, Po-10 and YP136 are summarized in Table 1.

113   The whole session lasted for 6 days. During the session, the machine ran automatically and

114   continuously without any attentions besides mount change and analytical chain defining. The analyses

115   of mount 1 and 2 pairs were conducted 1 time every day interspersed some other mounts with sample

116   YP136. The analyses of the mount 2 (lasting about 3 hours) was always followed those in the mount 1

117   (lasting about 4 hours) in quick succession. The primary standard for pyrite is UWPy-1 (Ushikubo *et al.*

118   2014) and pyrrhotite is Po-10 (Gilbert *et al.* 2014).

119   **3.2. Gas mass spectrometer**

120   The $\delta^{34}S$ value of YP136 was also determined by gas mass spectrometer at Beijing Research Institute

121   of Uranium Geology. YP136 pyrrhotite grains were handpicked under a binocular microscope and

122   pentlandite is avoided. The purity of each sample was greater than 98%. Pyrrhotite grains (about 0.4mm)

123   were mixed with cuprous oxide and crushed into 200 mesh powder. The SO_2 was produced through

124   reaction of sulfide and cuprous at 980 °C under a vacuum pressure of 2×10^{-2} Pa. The SO_2 was measured

125   by MAT-251 mass spectrometer. Measurement precision of all analysis, expressed by twice the

126   coefficient of variation, was better than ± 0.2% (2s).

127   **3.3. BSE photography and WDS mapping**

128   Polished mounts in this study were investigated with a ZEISS SUPRA 55 SAPPHIRE field emission

129   scanning electron microscope (SEM) in backscattered electron (BSE) mode at the State Key Laboratory

130   of Isotope Geochemistry, Guangzhou Institute of Geochemistry. The BSE data were collected by

131   automatic mapping at room temperature with step sizes of 10 μm.

132   Major elements of YP136 were determined using a JEOL JXA-8230 electron probe micro-analyzer

133   (EPMA) at the Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry.

134   Operating conditions were an accelerating voltage of 20 kV, a beam current of 20 nA and a 1 μm beam

135   were applied to the analyses for all elements. Elements and X-ray lines used for the analyses are Fe (Kα),

136   S (Kα), As (Lα), Se (Lα), Ni (Kα), Co (Kα), and Sb (Lα). The peak counting times were 30 s for Fe and

137   S; 60 s for As, Ni, and Co; 120 s for Se and Sb. In-house reference material used for calibration were

138   FeS_2 (for Fe and S), FeAsS (for As), Se (for Se), Ni (for Ni), Co (for Co) and Sb_2S_3 (for Sb).

139   Elemental mapping by wavelength dispersive spectrometry (WDS) was conducted using a JEOL

140   JXA-8230 electron probe micro-analyzer (EPMA) at the Key Laboratory of Mineralogy and Metallogeny,

141   Guangzhou Institute of Geochemistry. The operating conditions were an accelerating voltage of 20 kV,

142   a probe current of 50 nA and a beam size of 4 μm were adopted. Elements and X-ray lines used were Fe

143   (Kα), S (Kα), FeAsS (for As), Se (for Se), Ni (for Ni), Co (for Co) and CuS (for Cu). The step size was

144   4 μm and the dwell time was set to be 100 ms for each point.

145

146   **4.   RESULTS AND DISCUSSION**

147   Results of 6 measurements of PPP-1 and Po-10 in mount 1 and 2 pairs are displayed in Figure. 2. A

148   total of 180 PPP-1 (pyrite) and 120 Po-10 (pyrrhotite) spots were collected from the whole session.

149   **4.1. Mount to mount fractionation**

150   The difference of raw $\delta^{34}S$ values of PPP-1 in 6 days on mount 1 is no larger than 0.2‰ (9.3‰ to

151   9.5‰, Fig. 2a). The same difference is also observed on mount 2 (Fig. 2a). The difference of raw $\delta^{34}S$

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152   values of PPP-1 on mount 1 and 2 in the same day for the whole session is no larger than 0.1‰ (Fig. 2a).

153   A similar result is also observed for Po-10 (Fig. 2b). The small difference of raw δ^{34}S values of PPP-1

154   and Po-10 for different mounts in one day indicates that when analytical parameters are kept unchanged,

155   the IMF of pyrite and pyrrhotite was not affected by mount changing process and mount to mount

156   difference.

157   When calibrated using UWPy-1 in mount 1, both the result of PPP-1 in mount 1 and 2 show a

158   normal distribution and with a same peak value of 5.9‰ (5.89‰ ~ 5.87‰, Figs. 3a-b), which are

159   identical within the measurement repeatability precision, demonstrating the reliability of off-mount

160   calibration procedure. The δ^{34}S values of PPP-1 calibrated by UWPy-1 is slightly higher than the

161   accepted value of 5.3 ± 0.2‰ (2s, PPP-1) (Gilbert et al. 2014), this may indicate the slight heterogeneity

162   of this sample. Original data is given in online supporting information S1.

163   **4.2. YP136**

164   Based on the observation in Section 4.1, we calibrate all the raw value of sample YP136 by use of

165   the IMF value determined by the Po-10 in mount 1. The IMF-corrected data are shown in Figure 4a, and

166   the original data are given in online supporting information S2. The calibrated data show a normal

167   distribution with a peak value of 1.5‰ (Fig. 4b), and the small range of δ^{34}S values demonstrates

168   homogeneity of this sample. Usually, the homogeneity of one sample can be assessed by calculating the

169   mean square weighted deviation (MSWD) of repeated analyses. If MSWD ≤ 1, sample is considered

170   isotopically homogeneous within uncertainty (Gilbert et al. 2014). The MSWD of all YP136 spots is

171   0.75, indicating that the sulfur isotope of this sample is homogeneous within the measurement precision.

172   More details in online supporting information S3.

173   The YP136 sample were also repeated analyzed 11 times by gas mass spectrometer and the $\delta^{34}S$ value

174   ranges from 1.5 to 1.6‰, which yields an average of 1.5 ± 0.1‰ (2s, n=11). The detailed analytical

175   results are given in Table 2 and Figure 5. The average $\delta^{34}S$ value of YP136 pyrrhotite corrected by Po-

176   10 is 1.5 ± 0.3‰ (2s) and is in great agreement with the results derived by gas mass spectrometer.

177   Quantitative composition analysis of the YP136 pyrrhotite (n=40) shows that this sample is

178   composed of 60.9 ± 0.3 g/100g Fe, 38.6 ± 0.4 g/100g S, 0.54 ± 0.05 g/100g Ni, 0.07 ± 0.02 g/100g Co,

179   with trace amounts of Sb (~10 µg/g) and As (~20 µg/g) (Tab. 2). Combined with the WDS mapping of

180   this sample (Figs. 1d-e, Fig. 6), we think that the YP136 pyrrhotite is homogeneous in both major and

181   trace elements, though further LA-ICP-MS trace element analysis is needed to confirm this assertion.

182   According to the results presented in this study, the pentlandite exsolution and pyrite/chalcopyrite

183   intergrowths, if present, can be readily identified under microscope examination and can be easily

184   avoided during SIMS analysis.

185   **4.3. Triple sulfur isotope characteristic of PPP-1, Po-10 and YP136**

186   For sulfur isotope system, we usually define $\Delta^{33}S = 0$ as mass dependent fractionation (MDF,

187   Farquhar *et al.* 2000) and when $\Delta^{33}S$ exceeds the range of 0 ± 0.2‰ mass independent fractionation is

188   established (MIF, Ohmoto *et al.* 2006). The $\Delta^{33}S$ values of UWPy-1, PPP-1 pyrite and Po-10 lie in the

189   range of 0 ± 0.2‰ (Fig. 7), which is consistent with previous study (Fu *et al.* 2017, Ushikubo *et al.* 2014),

190   indicating they are sourced from MDF-S. However, most of the $\Delta^{33}S$ value of YP136 lies around +0.2‰

191   (up to +0.4‰, Fig. 7), which shows obvious MIF and is clearly different from other reference materials.

192   This result suggests MIF-S contribution for its formation. The MIF-S was found in samples older than

193   2.4 Ga and thought to be produced in anoxic Archean atmosphere (Farquhar *et al.* 2000). Given that the

194   PGE mineralized complex, from which the YP136 is collected, has an age of 2.44 Ga (Iljina *et al.* 2015),

195   it is possible that some of the sulfur in this deposit may eventually source from atmospheric sulfur.

196   Further gas-source mass spectrometry analysis is needed to confirm the potential MIF signature of YP136

197   pyrrhotite. Nevertheless, YP136 could potentially be a working reference material characterized by MIF

198   sulfur isotope anomaly which makes it not only a suitable standard to correct pyrrhotite samples with

199   MIF-S signature but also a good monitor to assure that the calculation procedures used in any given study

200   are correct.

201

202   **5. CONCLUSION**

203   In this study we have demonstrated that when CAMECA IMS 1280-HR keeps its analytical

204   parameters unchanged in 6 days, the IMF for sulfur isotope analysis of pyrite and pyrrhotite in different

205   sample mounts remains stable. This justifies off-mount calibration for pyrite and pyrrhotite during SIMS

206   sulfur isotope analysis. Sulfur isotope measurement by SIMS of one new pyrrhotite reference material

207   YP136 yield good homogeneity. The measurement repeatability of YP136 pyrrhotite during SIMS

208   analysis is typically 0.3‰ (2s). Combined with its chemical homogeneity, we think it has potential to be

209   a candidate reference material for *in-situ* micro analysis. YP136 was also characterized by gas mass

210   spectrometer in addition to the SIMS measurements. The average $\delta^{34}S$ value determined with gas mass

211   spectrometer for YP136 is 1.5 ± 0.1‰ (2s), which is identical to the results derived from SIMS

212   measurement, 1.5 ± 0.3‰ (2s). Grains of YP136 are available upon request.

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330   **FIGURE CAPTIONS**

331   **Fig. 1.** (a) hand specimen of YP136 pyrrhotite; (b) photomicrograph of YP136 pyrrhotite; (c) BSE image

332   of the same grain in Fig. 1b showing that the pyrrhotite is very clear with only minor pentlandite

333   exsolution; (d) WDS mapping of Fe; (e) WDS mapping of S. Abbreviations: Po: pyrrhotite, Pn:

334   pentlandite.

335   **Fig. 2.** (a) raw $\delta^{34}S$ value of PPP-1 pyrite on mount 1 and 2; (b) raw $\delta^{34}S$ value of Po-10 pyrrhotite on

336   mount 1 and 2. The uncertainties shown are measurement repeatability only.

337   **Fig. 3.** Frequency histogram of $\delta^{34}S$ values of PPP-1 on mount 1 (a) and mount 2 (b).

338   **Fig. 4.** (a) IMF-corrected $\delta^{34}S$ value of YP136 pyrrhotite determined by SIMS; (b) frequency histogram

339   of $\delta^{34}S$ values of YP136 pyrrhotite (n=318) in the whole session.

340   **Fig. 5.** The $\delta^{34}S$ values of YP136 pyrrhotite (n=11) determined by gas mass spectrometer.

341   **Fig. 6.** WDS mapping of trace elements (Ni, Co, Ni, Co, As, Se and Cu) in YP136 pyrrhotite.

342   **Fig. 7.** $\delta^{33}S$ vs $\delta^{34}S$ diagram with all samples analyzed in this study, note the insert figure showing $\Delta^{33}S$

343   of YP136.

344

345   **TABLE CAPTIONS**

346   **Table 1.** Typical $\delta^i S_{raw}$, α and $\delta^i S$ values of UWPy-1, PPP-1, Po-10 and YP136.

347   **Table 2.** Sulfur isotope analyses of YP136 pyrrhotite (n=11) by gas mass spectrometer.

348   **Table 3.** Major elements detected by EMPA (wt%).

349

350   **SUPPORTING INFORMATION**

351   **S1.** Original $^{34}S/^{32}S$ ratios of PPP-1, UWPy-1 and Po-10.

352   **S2.** Original $^{34}S/^{32}S$ ratios of YP136.

353   **S3.** MSWD of repeated spots on YP136.