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# Characterization of porosity in sulfide ore minerals: A USANS/SANS study

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## ABSTRACT

26 Porosity plays a key role in the formation and alteration of sulfide ore minerals, yet our knowledge  
27 of the nature and formation of the residual pores is very limited. Herein, we report the application of  
28 ultra small angle neutron scattering and small angle neutron scattering (USANS/SANS) to assess  
29 the porosity in five natural sulfide minerals (violarite, marcasite, pyrite, chalcopyrite, and bornite)  
30 possibly formed by hydrothermal mineral replacement reactions and two synthetic sulfide minerals  
31 (violarite and marcasite) prepared experimentally by mimicking natural hydrothermal conditions.  
32 USANS/SANS data showed very different pore size distributions for these minerals. Natural  
33 violarite and marcasite tend to possess less pores in the small size range (<100 nm) compared with  
34 their synthetic counterparts. This phenomenon is consistent with a higher degree of pore healing or  
35 diagenetic compaction experienced by the natural violarite and marcasite. Surprisingly, nm-sized  
36 (<20 nm) pores were revealed for a natural pyrite cube from La Rioga, Spain and the sample has a  
37 pore volume fraction of ~7.7%. Both chalcopyrite and bornite from the massive sulfide assemblage  
38 of the Olympic Dam deposit in Roxby Downs, South Australia were found to be porous with a  
39 similar pore volume fraction (~15%), but chalcopyrite tends to have a higher portion of nm-size  
40 pores centered at ~4 nm while bornite tends to have a broader pore size distribution. The specific  
41 surface area is generally low for these minerals ranging from 0.94 to 6.28 m<sup>2</sup> g<sup>-1</sup>, and the surfaces  
42 are generally rough as surface fractal behavior was observed for all these minerals. This  
43 investigation has demonstrated that USANS/SANS is a very useful tool for analyzing porosity in  
44 ore minerals. We believe that with this quantified porosity information a deeper understanding of  
45 the complex fluid flow behavior within the porous minerals can be expected.

46 **Key words:** SANS, USANS, sulfide ore minerals, porosity, mineral replacement reactions.

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## INTRODUCTION

48 Porosity is often an overlooked feature of all types of rocks and also within their constituent  
49 minerals. It plays an important role in a number of geological processes including metamorphism  
50 and metasomatism as it provides pathways for fluid flow and hence promotes fluid-rock interactions.  
51 Metasomatism is in fact the alteration of mineral assemblages by hydrothermal fluids and in the  
52 process one assemblage is replaced by another by dissolution-precipitation processes (Putnis,  
53 2002; Putnis, 2009). Such hydrothermal replacement processes are a dominant mechanism in the  
54 formation of most types of ore deposits in the Earth's crust. These mineral replacement reactions  
55 (and recrystallization reactions) require the generation of porosity in the product minerals, which  
56 may or may not decay or coarsen over time (See (Putnis et al., 2005); (Zhao et al., 2013)). The  
57 extent of remnant porosity preserved in the ores over geological time is a subject that does not seem  
58 to have been explored. Although the porosity in hydrothermally altered rocks has been investigated  
59 (Baumgartner et al., 1997; Norton and Knapp, 1977), the petrographical techniques used in these  
60 early studies were not able to measure very small pores.

61 Small angle neutron scattering (SANS) is a powerful tool for the characterization of porosity as it is  
62 non-destructive and requires only simple sample preparation. Different from gas adsorption or  
63 mercury intrusion techniques, which only measure accessible pores in a limited size range, SANS  
64 has the ability to characterize both accessible and inaccessible pores in a wider size range. The  
65 SANS technique can probe pore sizes from sub-micrometer down to sub-nanometer which is  
66 beyond the resolution of scanning electron microscopy. As it measures bulk samples, it can give a  
67 good average picture of the porosity on a large scale ( $\text{cm}^3$ ). With the increasing availability of ultra  
68 small angle neutron scattering (USANS) instruments, the pore size range that can be characterized  
69 has been extended up to 10s of micrometers. Porosity characterization using combined  
70 USANS/SANS is hence a particularly powerful tool for geological samples because these materials  
71 often exhibit a wide range of pore sizes. In recent years, there have been a few successful  
72 USANS/SANS studies investigating the porosity in sedimentary rocks (Anovitz et al., 2013a;

73 Anovitz et al., 2010; Clarkson et al., 2013; Jin et al., 2011), metamorphic rocks (Anovitz et al., 2009;  
74 Wang et al., 2013), igneous rocks (Navarre-Sitchler et al., 2008; Navarre-Sitchler et al., 2013), coals  
75 (Sakurovs et al., 2012), and single-crystal beryl (Anovitz et al., 2013b), but no USANS/SANS  
76 studies have been reported on sulfide ores or ore minerals.

77 Over the last few years, we have undertaken extensive investigations into the mechanism and  
78 kinetics of hydrothermal mineral replacement reactions related to ore formation under conditions  
79 that mimicking natural ore-forming environments. In all cases the product mineral showed evidence  
80 of reaction generated porosity. The ore-forming reactions that have been studied include the  
81 replacements of pentlandite by violarite (Tenailleau et al., 2006; Xia et al., 2009; Xia et al., 2008;  
82 Xia et al., 2007), pyrrhotite by marcasite and pyrite (Qian et al., 2011; Xia et al., 2010; Xia et al.,  
83 2007), hematite by chalcopyrite (Zhao et al., 2014b), chalcopyrite by bornite (Zhao et al., 2014a),  
84 magnetite by pyrite (Qian et al., 2010) and by arsenian-pyrite (Qian et al., 2013), calaverite by gold  
85 (Zhao et al., 2009; Zhao et al., 2010), and sylvanite and krennerite by gold-silver alloy (Xu et al.,  
86 2013; Zhao et al., 2013). In all these replacement reactions, porosity was generated in the daughter  
87 minerals regardless whether the reaction involves volume contraction or expansion. Nevertheless,  
88 microscopic evidence showed a difference in pore textures from different replacement reactions  
89 (Brugger et al., 2010). Aiming to improve our understanding of the nature and extent of porosity in  
90 sulfide minerals, we undertook this USANS/SANS study in order to characterize remnant porosity  
91 in some natural sulfide ores, and the porosity generated in the sulfides obtained experimentally via  
92 hydrothermal replacement reactions (Table 1). In selecting the natural sulfide minerals we focused  
93 on samples which were thought to have been forming by solution driven hydrothermal replacement  
94 reactions and thus we are seeking textural evidence in the form of remnant porosity for the  
95 replacement mechanism.

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## EXPERIMENTAL METHODS

98 USANS/SANS curves of powdered samples were measured in this study (Table 1). The samples  
99 were crushed and sieved to powders (20-53  $\mu\text{m}$  for natural samples or 63-150  $\mu\text{m}$  for synthetic  
100 samples) and then the powders were loaded into sample cells. The sample cells consist of a metal  
101 framework, with a pair of identical quartz windows 25 mm in diameter and 1 mm in thickness and a  
102 polytetrafluoroethylene (PTFE) ring (ID 20 mm, OD 25 mm, and thickness 100  $\mu\text{m}$ ) fixed to one of  
103 the quartz windows by adhesive tape to provide a defined sample edge. The thickness of the PTFE  
104 ring plus the adhesive tape was  $\sim 200$   $\mu\text{m}$ . A known weight of powdered sample was evenly  
105 distributed within the PTFE ring to form a flat disk with the aid of acetone flooding. The sample  
106 was left to dry for 15 min for complete acetone evaporation, which was confirmed by comparing  
107 weight before acetone flooding and after evaporation. Then the thickness of the sample was  
108 carefully measured with a micrometer by placing a thin flat aluminum disk on top of the sample.  
109 The thickness of the sample was accurately established by subtracting the thicknesses of both the  
110 quartz window and the aluminum disc. Finally the second quartz window was placed on top of the  
111 sample and the assembled cell was loaded vertically onto the cell holders at the sample position of  
112 SANS or USANS instruments. The sample thickness can be slightly thinner or thicker than the  
113 PTFE ring without powder collapse during experiments. The measured thicknesses of the samples  
114 are in the range 100-500  $\mu\text{m}$  (Table 2), which is thin enough to avoid multiple scattering but thick  
115 enough to maintain sufficient scattering power.

116 SANS measurements of chalcopyrite and pyrite samples were carried out at the 40 m pinhole SANS  
117 instrument (Quokka) (Gilbert et al., 2006), at Australian Nuclear Science and Technology  
118 Organisation (ANSTO) using a wavelength of 5  $\text{\AA}$  and a sample aperture size of 15 mm in diameter.  
119 Three sample-to-detector distances (2.11 m, 6.11 m, and 20.09 m) were employed, covering a Q  
120 range from 0.004  $\text{\AA}^{-1}$  to 0.33  $\text{\AA}^{-1}$ . SANS measurement of the other samples were carried out on the  
121 40 m pinhole SANS beam line at Korea Atomic Energy Research Institute (KAERI) (Han et al.,  
122 2013), using a wavelength of 6  $\text{\AA}$  and a sample aperture size of 12 mm in diameter. Three sample-

123 to-detector distances (1.16 m, 5.7 m, and 13.7 m) were used covering a Q range from  $0.0033 \text{ \AA}^{-1}$  to  
124  $0.47 \text{ \AA}^{-1}$ . USANS measurements of all samples except synthetic violarite were carried out on the  
125 perfect crystal silicon triple Bragg instrument S18 beam line (Hainbuchner et al., 2000; Kroupa et  
126 al., 2000), at Institut Laue-Langevin (ILL), Grenoble, France, using a neutron wavelength of  
127  $\lambda=1.95\pm 0.03 \text{ \AA}$  (Q range:  $1.6\times 10^{-5} \text{ \AA}^{-1}$  to  $0.0016 \text{ \AA}^{-1}$ ) and a sample aperture size of 16 mm in  
128 diameter. USANS of the synthetic violarite sample was measured at the newly installed quintuple-  
129 bounce perfect silicon crystal USANS instrument (Kookaburra) (Rehm et al., 2013) at ANSTO  
130 using a neutron wavelength of  $4.74 \text{ \AA}$  (Q range:  $2.78\times 10^{-5} \text{ \AA}^{-1}$  to  $0.005 \text{ \AA}^{-1}$ ) and a sample  
131 aperture of 19 mm in diameter. The SANS data of all our samples are isotropic and the 1-D  
132 scattering patterns were obtained by radial averaging of the 2-D raw data. The SANS data were  
133 calibrated to the absolute scale by the empty beam method using the NIST package (Kline, 2006).  
134 The slit smeared USANS data was corrected by a de-smearing process (Schmidt, 1965; Schmidt  
135 and Hight, 1960), and the normalized data were merged with the absolute calibrated SANS data.  
136 The combined USANS/SANS curves probe a broad range of characteristic pore sizes (R) ranging  
137 from 0.6 nm to  $15.6 \mu\text{m}$  (estimated using  $R=2.5/Q$ ; (Radlinski et al., 2000)).

138 The characterization of pore size and fraction of the same samples was undertaken using either a  
139 Quanta 450 field emission Scanning Electron Microscope (SEM) or a FEI Helios high resolution  
140 SEM at Adelaide Microscopy, University of Adelaide. The samples were embedded in epoxy resin  
141 and the surfaces were polished with diamond paste and then coated with a carbon film to avoid  
142 electron charging. The Quanta 450 SEM examination was performed at 20 kV accelerating voltage,  
143 0.34 nA specimen current, and 4.0 mm working distance. The FEI Helios SEM examination was  
144 performed at 5.0 kV accelerating voltage, 0.34 nA specimen current, and 4.0 mm working distance.

#### 145 **USANS/SANS DATA ANALYSIS**

146 The main purpose of data analysis is to obtain porosity information for the samples. Specifically,  
147 we aim to determine the specific surface area, fractal dimension, pore volume fraction, and pore  
148 size distribution. The Irena (v2.52) software was used for data fitting and analysis (Ilavsky and

149 Jemian, 2009). The sample thickness was optimized to minimize multiple scattering and this greatly  
150 simplifies data interpretation. Multiple scattering effects were negligible as (1) transmission of all  
151 samples were greater than 90% (Table 2) and (2) measurements of two thicknesses of the same  
152 sample resulted in overlapping SANS curves. A brief description of the theory behind the data  
153 analysis is provided below.

154 In small angle scattering, the scattering intensity  $I$  is expressed as a function of wave vector transfer  
155  $Q$ , which is written as,

$$156 \quad Q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (1)$$

157 where  $\lambda$  is the neutron wavelength and  $\theta$  is the scattering angle (Garvey et al., 2013). In many cases,  
158 a power law, in which scattering intensity is proportional to a negative power of  $Q$ , can be used to  
159 model the scattering curves (Guinier and Fournet, 1955; Radlinski, 2006),

$$160 \quad I(q) = Aq^{-\alpha} + B \quad (2)$$

161 Here the slope of a log-log plot of the data gives the power exponent  $\alpha$ . In this equation,  $A$  is a  
162 contrast-dependent constant, and  $B$  is the contribution from incoherent scattering.

163 From the power exponent  $\alpha$ , the geometry of the scatterer can be deduced (Schmidt, 1991). For  
164 example,  $\alpha=1$  indicates thin rods or filaments,  $\alpha=2$  indicates thin platelets,  $\alpha=1.67$  and  $2<\alpha<3$  may  
165 refer to mass fractal structures (3D self similarity over a large range of length scales),  $3\leq\alpha<4$   
166 corresponds to surface fractal structures (rough surface with self similarity over a large range of  
167 length scales), and  $4<\alpha<5$  suggests a non-fractal “fuzzy” interface with a varying scattering length  
168 density between two phases (Anovitz et al., 2009). If  $\alpha=4$ , Equation (2) becomes the Porod law  
169 (Porod, 1951), which is applied to 3-dimensional objects with sharp and smooth surface. For  
170  $3\leq\alpha<4$ , the surface fractal dimension  $D_s$  can be calculated,  $D_s = 6 - \alpha$ .

171 The volume fraction occupied by the pores  $\Phi$  (porosity) can be determined from the scattering  
172 invariant  $Y$ , which represents the total scattering power of the sample and it is evaluated by  
173 integrating the observed intensity  $I(Q)$  over the whole reciprocal space (Porod, 1952),

$$174 \quad Y \equiv \int_0^{\infty} Q^2 I(Q) dQ = 2\pi^2 (\Delta\rho)^2 \varphi(1 - \varphi) \quad (3)$$

175 To minimize the contribution from inter-particle pore volumes due to close packing of powder  
176 samples, care was taken in  $Q$ -range selection for scattering-invariant calculations. For example, for  
177 particle size range 20-53  $\mu\text{m}$ , the smallest inter-particle pore diameter is around  $\sim 1.5 \mu\text{m}$   
178 ( $Q = 1.62 \times 10^{-4} \text{ \AA}^{-1}$ ) assuming close packing of spheres. So, data points  $Q < 1.62 \times 10^{-4} \text{ \AA}^{-1}$  were  
179 excluded in the calculation of scattering invariant.

180 The size distributions of the samples were modeled using the maximum entropy method (Jemian et  
181 al., 1991; Potton et al., 1988a; Potton et al., 1988b), which utilizes a regularization approach  
182 employing the following formula:

$$183 \quad I(Q) = (\Delta\rho)^2 \sum F(Q, r)^2 V^2(r) NP(r) dr, \quad (4)$$

184 where  $F(Q, r)$  is the scattering form factor,  $V(r)$  is the volume of a particle of diameter  $r$ ,  $N$  is the  
185 total number of scattering particles, and  $P(r)$  is the unknown probability distribution of particle  
186 sizes, and  $(\Delta\rho)^2$  is the scattering contrast, which is the square of the difference in scattering length  
187 density  $\rho$  between the solid mineral phase and the pore ( $\sim 0$  for air).  $\rho$  can be calculated from the  
188 chemical composition and phase density,

$$189 \quad \rho = N_A d \sum_i s_i b_i / \sum_i s_i M_i \quad (5)$$

190 where  $N_A$  is Avogadro's constant,  $d$  is the phase density,  $s_i$  is the proportion by number of nucleus  $i$   
191 in the mineral,  $M_i$  is its atomic mass, and  $b_i$  is the coherent scattering amplitude for nucleus  $i$ . The  
192 calculated  $\rho$  of the mineral samples are listed in Table 2.

193 Here a data binning and interpolation process was applied to the original data and the processed  
194 data that was used for size distribution fitting. This is because the original data points are very  
195 unevenly spaced due to limited USANS data points (Figure 1). The processed data after binning  
196 consists of 300 evenly spaced (log-scale) points better suited for the mathematical model used in the  
197 size distribution fitting.

198 A spherical form factor was assumed, and the fitting was converged when the configurational  
199 entropy of the size distribution was maximized. Log-normal size distribution was obtained by  
200 fitting the scattering calculated from the trial distributions to the data.



201 The specific surface area per unit volume  $S_v$  was calculated from size distribution data. The specific  
202 surface area per unit mass  $S_m$  was then calculated by dividing  $S_v$  by the packing density  $d_p$ ,

$$203 \quad S_m = \frac{S_v}{d_p} \quad (6)$$

204 Here the packing density  $d_p$  was calculated by dividing sample weight by the occupied cell volume  
205 (Table 2).

## 206 RESULTS AND DISCUSSION

### 207 USANS/SANS curves

208 The combined USANS/SANS curves are shown in Figure 1. All samples scatter in the entire  $Q$   
209 range from  $1.6 \times 10^{-5} \text{ \AA}^{-1}$  to  $0.47 \text{ \AA}^{-1}$ , indicating a very broad distribution of scatterer size. This is a  
210 very common USANS/SANS feature for geological samples as was observed in many rocks  
211 (Anovitz et al., 2013a; Anovitz et al., 2009; Clarkson et al., 2013; Jin et al., 2011; Navarre-Sitchler  
212 et al., 2008; Navarre-Sitchler et al., 2013) and coals (Sakurovs et al., 2012). The USANS/SANS  
213 curves have a flat tail at the high  $Q$  region, which are probably due to incoherent scattering from  
214 absorbed moisture on the sample surface or trapped in fluid inclusions (pores) within the mineral  
215 grains. The  $Q$  range for the flat tail is similar for all samples with the tail starting from  $Q \approx 0.06$   
216 (Fig. 1). During data analysis the flat tail was subtracted as the background (the parameter  $B$  in  
217 Equation 2). The results from data analysis are summarized in Table 2. A detailed discussion of  
218 these results for individual samples is provided in the following paragraphs.

### 219 Natural and synthetic violarite

220 In Nature violarite ( $\text{Ni}_2\text{FeS}_4$ ) forms as a supergene replacement product of pentlandite ( $(\text{Ni,Fe})_9\text{S}_8$ )  
221 under the action of hydrothermal fluids (Nickel et al., 1974; Thornber, 1975). The process was  
222 reproduced experimentally by (Xia et al., 2009; Xia et al., 2008). This replacement reaction  
223 involves a theoretical volume reduction of  $\sim 16.8\%$  assuming the conservation of sulfur. The  
224 calculated pore volume ( $< 1.8 \mu\text{m}$ ) fractions for both the natural violarite (18.1%) and synthetic  
225 violarite (18.7%) are very close but slightly higher than the theoretical value. This higher volume  
226 reduction may be due to (1) the expanded cracks as a result of thermal expansion at the reaction

227 temperature (120 °C for the synthetic sample) and this expanded crack did not contract after cooling  
228 to room temperature, and (2) some loss of S to the solution.

229 Pore size distributions (Fig. 2a) show that synthetic violarite has a larger portion of small pores  
230 (<100 nm) than natural violarite. Microscopic sample texture for partially reacted natural and  
231 synthetic violarite show quite similar pore size range (Fig. 2b & c), but pores <100 nm were not  
232 observable in the SEM images. The very similar pore volume fraction and the microscopic texture  
233 are consistent with the similarity of formation mechanism for synthetic and natural violarite – the  
234 coupled dissolution-precipitation mineral replacement reactions (Xia et al., 2009); and the lower  
235 fraction of small pores in natural violarite may be due to the pore healing or later precipitation  
236 processes over an extended time in the supergene environment. The fine pores initially formed can  
237 be healed or coarsened over time driven by minimization of surface energy (Putnis et al., 2005).

238 Both samples have the surface fractal feature (Table 2), which is very common for rocks (Anovitz  
239 et al., 2009; Kahle et al., 2006). The difference between natural and synthetic violarite lies in that  
240 synthetic violarite tends to be rougher in the small size range (higher  $D_s$  value in the SANS region)  
241 but smoother in the large size range (lower  $D_s$  value in the USANS region). The specific surface  
242 area is  $3.36 \text{ m}^2 \text{ g}^{-1}$  for natural violarite and  $6.28 \text{ m}^2 \text{ g}^{-1}$  for synthetic violarite (Table 2).

#### 243 **Natural and synthetic iron disulfides (marcasite and pyrite)**

244 Pyrite and marcasite are polymorphs of iron disulfides ( $\text{FeS}_2$ ) and are closely associated in Nature.  
245 Evidence has shown that marcasite is often a daughter mineral after pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) by mineral  
246 replacement reaction (Fleet, 1978). In Nature marcasite is metastable and can be converted to pyrite,  
247 which is the more thermodynamically stable form (Fleet, 1970; Lennie and Vaughan, 1992). Here  
248 we report the porosity for the three iron disulfide samples - natural pyrite, natural marcasite, and  
249 synthetic marcasite.

250 The pyrite sample shows 7.7 % porosity (<1.7  $\mu\text{m}$ ). This is surprisingly high, since the sample was  
251 from a relatively large and well-formed cube ( $\sim 1 \text{ cm}^3$ ) from the famous deposit near Navajún, La  
252 Rioja, Spain. One might expect minimum or no porosity. The pyrite has a surface area of  $3.56 \text{ m}^2 \text{ g}^{-1}$

253 <sup>1</sup>, which is also too high for a dense mineral. To confirm the pore existence, we measured the  
254 density of the sample. The measured density, 4.813 g cm<sup>-3</sup>, is indeed lower than the theoretical  
255 density 5.04 g cm<sup>-3</sup> calculated from the unit cell dimension (Paszkwicz and Leiro, 2005). The  
256 porosity calculated from the density data is 5.6 % assuming the pores are filled with water. From  
257 size distribution (Fig. 3a) we see a large portion of small pores (<20 nm) which are not observable  
258 by SEM (Fig. 3b). It seems likely that these nm- sized pores were formed during crystal growth.  
259 The pyrite cubes at Navajún are believed to be formed by the hydrothermal sulfidation of chlorites  
260 in the marl, and the crystals can contain remnant chloritoid inclusions (Lodders et al., 1998).  
261 Reduced sulfur was supplied largely by thermochemical reduction of sulfate, with a small amount  
262 coming from sedimentary sulfides during metamorphism. The peak temperature during  
263 metamorphism is 370 °C (Alonso-Azcarate et al., 1999), thus these crystals are essentially  
264 hydrothermal in origin and formed by replacement reactions. All replacement reactions generate  
265 porosity to facilitate fluid flow and mass transport and it appears that even over extended periods of  
266 geological time (the crystals are thought to be formed possibly in the Cretaceous period; (Alonso-  
267 Azcarate et al., 1999)), the remnant porosity persists.

268 The replacement of pyrrhotite by marcasite involves a theoretical volume reduction of ~29% under  
269 oxidation condition assuming the conservation of sulfur (Fleet, 1978; Qian et al., 2011). For the  
270 synthetic marcasite, the pore volume calculated from scattering invariant was only 14.3%, but this  
271 porosity accounts only for size up to ~1.8 μm. SEM images also reveal larger pores/fractures  
272 (Fig. 3c), so obviously the populations of large pores and fractures accounts for the other half of the  
273 volume contraction. The size distribution (Fig. 3a) shows a large portion of small pores (<100 nm),  
274 which results in a relatively high specific surface area (5.98 m<sup>2</sup> g<sup>-1</sup>).

275 Compared with the synthetic marcasite, the natural marcasite sample shows a larger bulk porosity  
276 of 24.5 % in the same size range (<1.8 μm), and a different size distribution profile. The majority of  
277 pore volume in natural marcasite is contributed from large pores and there is very limited volume of  
278 small pores below 100 nm. Such high porosity suggests that this natural marcasite may be the

279 replacement product of pyrrhotite. The limited small pore volume results in a very low specific  
280 surface area ( $0.94 \text{ m}^2 \text{ g}^{-1}$ ) and may be due to the pore healing process (Putnis et al., 2005) or due to  
281 the diagenetic compaction process. SEM analysis revealed some large pores randomly distributed in  
282 the sample (Fig. 3d).

283 All three samples have surface fractal features and the surface fractal dimension  $D_s$  is in the range  
284 2.13-2.60 (Table 2). Generally, the surface of the natural marcasite is smoother than natural pyrite  
285 and synthetic marcasite.

### 286 **Chalcopyrite and bornite**

287 Chalcopyrite and bornite are essentially hydrothermal minerals and are often found together.  
288 Bornite is known to replace chalcopyrite (Halbach et al., 1998) and chalcopyrite has also been  
289 documented to form by the replacement of bornite (Augustithis, 1995). The chalcopyrite and  
290 bornite samples in this study are from the same mineral assemblage, the Olympic Dam mine, Roxby  
291 Downs, South Australia.

292 Pore volumes calculated from the scattering invariant up to pore size of  $1.7 \mu\text{m}$  are similar for  
293 chalcopyrite (14.2%) and bornite (15.0%). However, from pore size distribution profiles (Fig. 4),  
294 chalcopyrite has a larger portion of nm-sized small pores centered at  $\sim 4 \text{ nm}$  and bornite tends to  
295 have a broader distribution. For pores larger than  $100 \text{ nm}$ , both sample share a similar size  
296 distribution profile. Such size distribution results in a higher specific surface area of  $2.73 \text{ m}^2 \text{ g}^{-1}$  for  
297 chalcopyrite compared with bornite ( $0.99 \text{ m}^2 \text{ g}^{-1}$ ). Both samples have rough surface ( $D_s \approx 2.5$ ) at  
298 large sizes, but chalcopyrite changes to a smooth surface ( $D_s = 2.0$ ) at small sizes.

299 These porosity features in this case do not distinguish the parent mineral from the daughter mineral  
300 if replacement reaction ever took place. It is likely that the copper iron sulfide minerals at Olympic  
301 Dam originally formed by the replacement of hematite, and have subsequently been remobilized  
302 (Haynes et al., 1995). Recently Zhao et al (2014a) was able to form chalcopyrite and bornite by  
303 replacement of hematite under hydrothermal conditions. Again it is a surprising feature that these

304 nominally massive sulfide ore minerals have a relatively high porosity, which is indicative of their  
305 formation by hydrothermal replacement processes.

306

#### IMPLICATIONS

307 We have demonstrated that combined USANS/SANS measurement on sulfide ore minerals can  
308 provide rich porosity-related information including specific surface area, pore volume fraction, pore  
309 size distribution, as well as fractal dimensions. These properties are important input values for  
310 assessing fluid transport ability, which is of vital importance to a deeper understanding of the  
311 mechanism and kinetics of fluid mediated mineral alteration as well as metal transportation  
312 behavior within the porous ore minerals. A clearer understanding of mineral porosity will also  
313 benefit mineral exploration and processing. Another feature of USANS/SANS which we did not  
314 explore in this study is the capability to do contrast matching experiments, from which accessible  
315 pores can be distinguished from inaccessible pores. With this important information, fluid transport  
316 behavior within the porous minerals can be predicted more reliably (e.g., Sakurovs et al. 2012).

317

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501 **Figure captions**

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503 **FIGURE 1.** Combined USANS/SANS curves of (a) synthetic and natural violarite, (b) natural pyrite,  
504 and natural and synthetic marcasite, and (c) natural bornite and chalcopyrite. Detailed sample  
505 descriptions are provided in Table 1.

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507 **FIGURE 2.** (a) Volume distribution of scatterer size for synthetic violarite and natural violarite; SEM  
508 image of the cross-section of (b) natural violarite, and (c) synthetic violarite.

509

510 **FIGURE 3.** (a) Volume distribution of scatterer size for natural pyrite, natural marcasite, and  
511 synthetic marcasite. SEM images of (b) natural pyrite, (c) synthetic marcasite, and (d) natural  
512 marcasite.

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514 **FIGURE 4.** Volume distribution of scatterer size for chalcopyrite and bornite; SEM image of the  
515 cross-section of (b) chalcopyrite, and (c) bornite.

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## Tables

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**Table 1.** Summary of natural and synthetic mineral samples

Sample	Mineral name	Size ( $\mu\text{m}$ )	Comments
NVO	Natural violarite	20-53	Cosmos Ni Deposit, 40 km north of Leinster, Western Australia (SA Museum specimen G30330).
SVO*	Synthetic violarite	63-150	After synthetic pentlandite. For synthesis details see Xia et al. (2008, 2009).
NMA	Natural marcasite	20-53	Dal'Negorsk ore field in the Primorskiy Kraj district, Far Eastern Region, Russia (SA Museum specimen G27438).
SMA*	Synthetic marcasite	63-150	After a massive natural pyrrhotite from Kambalda, Western Australia. Synthesis condition is the same as Sample S1 in Qian et al. (2011).
PY	Natural pyrite	20-53	Pyrite cube from La Rioga, Spain.
BO	Natural bornite	20-53	Massive bornite-chalcopyrite-hematite mineral assemblage from the Olympic Dam mine, Roxby Downs, South Australia (SA Museum specimen G19341).
CH	Natural chalcopyrite	20-53	Massive bornite-chalcopyrite-hematite mineral assemblage from the Olympic Dam mine, Roxby Downs, South Australia (SA Museum specimen G19341).

\*Synthetic samples were sized before reactions and used for USANS/SANS without further grinding.

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526 **Table 2.** Summary of USANS/SANS results

Sample	Scattering length density $\rho$ ( $10^{10} \text{ cm}^{-2}$ )	Sample thickness ( $\mu\text{m}$ )	Transmission (%)	Packing density ( $\text{g cm}^{-3}$ )	Incoherent background ( $\text{cm}^{-1}$ )	Porosity	Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ )	$D_s$ (USANS)	$D_s$ (SANS)
NVO	3.91	320	94.83	1.1131	0.0437	0.181	3.36	2.38	2.53
SVO	3.91	330	93.66	1.0900	0.0459	0.187	6.28	2.14	2.76
NMA	3.71	253	95.21	1.3928	0.0132	0.245	0.94	2.13	2.18
SMA	3.71	330	93.96	1.0794	0.0436	0.143	5.98	2.47	2.60
PY	3.81	115	93.36	1.1902	0.0286	0.077	3.56	2.51	2.55
BO	3.62	215	93.12	1.7352	0.0062	0.150	0.99	2.48	2.25
CH	3.15	170	93.01	0.8987	0.0097	0.142	2.73	2.45	2.00

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