1   **Revision 1**

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3   **Australian sedimentary opal-A and its associated minerals: Implications for natural silica**

4   **sphere formation**

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9   **ABSTRACT**

10   The vast majority of precious opal on the world market comes from opal fields in the Great

11   Artesian Basin of Australia pointing to very special prerequisites for amorphous silica to consolidate in

12   a way that leads to the famous play-of-color. We analyzed twenty opal-A samples from the Andamooka

13   (South Australia) and Yowah (Queensland) precious opal fields, using petrographic microscopy, XRPD,

14   SEM, and EPMA in order to identify and characterize opaline silica, the mineral assemblage, and the

15   host rock. Opal-A consists of submicrometer-sized silica spheres with an average diameter of 140-

16   320 nm. The average diameter of monodisperse spheres is 140-290 nm with a relative standard

17   deviation (RSD) of less than 6%. Polydisperse spheres show an average diameter of 160-320 nm with a

18   RSD larger than 10%. This dichotomy in size is reflected by the Na/K ratio at both localities.

19   Monodisperse spheres show values below 1.2 while polydisperse ones show a ratio larger than 3.0,

20   whereas other contaminations with higher valence show no correlations at all. We therefore suggest that

21   the jump in Na/K signals a fundamental change of pH and salinity of the silica-bearing mineralizing

22   fluids. Judging from the pH stability of the host rock minerals with predominating alunite, kaolinite,

23   illite and gypsum, and omnipresent barite and anatase we conclude that the dominant late-stage

24   mineralization leading to precious opal happened at acidic pH. Our findings indicate that the host rocks

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25 and associated minerals are the key to unravel the complex history of opal-forming solutions. A

26 quantitative opal classification based on sphere diameters and their variability, decoupled from

27 gemological properties, is to be established.

28

29 **Keywords:** Opal-A, mineral chemistry, host rock, sphere size distribution, petrogenesis, Australia

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31   **INTRODUCTION**

32   Opal-A is a non-crystalline form of hydrous silica ($SiO_2 \times nH_2O$) that often consists of

33 submicrometer-sized spheres. In precious opal-A, monodisperse spheres with a diameter of about

34 150-350 nm form a regular three-dimensional array that diffracts visible light, giving the characteristic

35 play-of-color (Jones et al. 1964; Sanders 1964), which is absent in common opal-A. However, there are

36 many factors that can suppress this optical effect in common opal, even if composed of monodisperse

37 spheres in regular arrangements, notably: sphere sizes too small or too large, strong cementation of

38 spheres, or an unsuitable contrast between the respective refractive indices of spheres and cement

39 (Sanders 1964; Darragh et al. 1966). A quantitative opal classification distinguishes between

40 monodisperse spheres and those with a broad sphere size distribution. While the synthesis of silica

41 colloids with a narrow sphere size distribution is among the better characterized processes in materials

42 science (e.g., Iler 1979; Xia et al. 2000; and references therein), the factors controlling sphere diameter

43 and dispersity in geological systems are still a matter of debate.

44   Precious opal-A at Andamooka (South Australia) and Yowah (Queensland) is associated with the

45 deeply weathered Early Cretaceous sediments of the Marree Subgroup and Winton Formation,

46 respectively (Senior et al. 1977; Barnes et al. 1992). From the Late Cretaceous to Early Miocene,

47 weathering of feldspar, mica, and clay minerals liberated silica into solution that migrated over short to

48 moderate distances (Darragh et al. 1966; Barnes et al. 1992). Silica-laden solutions were trapped within

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49   about 40 m beneath the surface in voids, cracks and along groundwater permeability barriers e.g.,

50   kaolinitic sandstone overlying less permeable claystone. Slow evaporation gradually supersaturated

51   these trapped solutions, eventually leading to precipitation of amorphous silica and formation of

52   opal-A.

53   The precipitation of opal-A from solution is predominantly dependent on the degree of

54   supersaturation, ionic strength, and pH. At ambient conditions and pH <9, the solubility of amorphous

55   silica is ~100-150 ppm, with a maximum at pH 2-3 and a minimum around 7 (Alexander et al. 1954;

56   Iler 1979). Electrolytes generally reduce the solubility, with polyvalent cations being more effective

57   than monovalent ones (Marshall and Warakomski 1980; Crerar et al. 1981). From supersaturated

58   solutions, particles grow by addition of silica monomers and polymers on the surface or by aggregation

59   with other solid particles (e.g., Bogush and Zukoski 1991; Icopini et al. 2005). Spheres in opal-A

60   consist of 25-40 nm-sized subparticles (Darragh et al. 1966; Jones and Segnit 1971; Gaillou et al.

61   2008b) and are most likely to form by an aggregative growth process. Experiments and modeling on

62   silica colloid formation from natural hydrothermal brine solutions show that particles with a diameter

63   of 30-40 nm are aggregates of nanoparticles ~3 nm in size (Icopini et al. 2005; Conrad et al. 2007).

64   These small particles have not been reported for natural opal so far. The surface properties of silica

65   particles are fundamental to colloid stability and strongly depend on solution pH and salinity. Above

66   the isoelectric point (IEP) at about pH 2-3, particles carry a negative surface charge that increases with

67   pH because of surface silanol dissociation. As a result, the colloid should be stable at high pH and

68   unstable at low pH, where spheres exhibit little or no surface charge. Silica particles smaller than a few

69   hundred nanometers act differently. They exhibit a local stability maximum at the IEP and a minimum

70   around pH 6 (Iler 1979; Kobayashi et al. 2005; Conrad et al. 2007). In electrolytes, counter-ions

71   accumulate close to the negatively charged particle surface and form a diffuse electrical double-layer

72   whose extent $1/\kappa$ is inversely proportional to the square root of the ionic strength. When particles

73   approach, their double-layers overlap and repulse each other.

74   On the basis of pH and salinity, Stewart et al. (2010) calculated, that monodisperse spheres, as in

75   opal-A, self-assemble by electrostatic forces into an ordered array at pH 9-10 and c_{NaCl} 10^{-3}-10^{-4} M.

76   This result contradicts the assumption of opal formation at neutral to mildly acidic pH and the common

77   opinion of gravity-driven sorting of slowly sedimenting uniform spheres (Iler 1965; Darragh et al.

78   1966; Gaillou et al. 2008b). In contrast, Piret and Su (2008) synthesized self-assembled arrays of

79   monodisperse silica spheres from tetraethylorthosilicate at pH 1-3 and 10 with c_{NaCL} 10^{-2}-5×10^{-2} M.

80   Noting the difference between calculations and experiments, clarification of the relevant solution

81   characteristics is needed to understand natural opal formation. The parent solutions of the two types of

82   Australian opal are unknown, and their properties and qualities can only be deduced from indirect

83   observations such as the assemblage of coexisting minerals and their stability depending on pH and

84   solution composition. We investigate the relation between sphere size distribution and chemical

85   composition of natural opal. This is a further step towards a better understanding of opal formation in a

86   sedimentary setting.

87

88   **MATERIALS AND ANALYTICAL METHODS**

89   **Sample origin and acquisition**

90   Sixteen samples from Andamooka (South Australia) and four samples from Yowah (Queensland)

91   were investigated using a number of methods, in order to identify and characterize opaline silica, the

92   mineral assemblage, and the host rock (Table 1). Samples were collected in the Teatree Flat field

93   located about 15 km northwest of the Andamooka Township and from different locations within the

94   Yowah opal field located a few kilometers south of the town of Yowah. All samples were transported in

95   sealed polyethylene bags until further preparation. The host rock and silicified samples from

96   Andamooka were extracted from bulldozer cuts about 20 m beneath the surface, in close proximity to

97   the layer (named "level" by the miners) in which most precious opal is found. Silicified samples from

98   Andamooka consist of sediments (mudstones, conglomerates, an opal breccia, and a silicified pebble),

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99   mollusc shell pseudomorphs, and coniferous wood (Fig. 1). Samples from Yowah are spherical

100 siliceous ironstone nodules. Opals analyzed include gray, white, light brown, colorless, and transparent

101 honey-colored samples. All specimens were stored in sealed polyethylene boxes between analyses to

102 prevent exsiccation. Procedures for sample and specimen preparation are described in detail below.

103 **Thin section preparation and optical petrography**

104   Opals and silicified sediments were cut using a 10" diamond-impregnated steel lapidary saw,

105 which was cooled by tap water. Friable porous samples were cut using a 5" diamond-impregnated steel

106 lapidary saw cooled with water-free Isocut Fluid (Buehler). These specimens were subsequently rinsed

107 with acetone to remove debris and cut fluid, dried overnight in an oven at 35 °C and embedded in

108 epoxy resin prior to lapping and finishing. Polished thin sections of standard dimensions (~26×48 mm

109 at ~30 μm thickness) were prepared using standard procedures. Specimens were cleaned between

110 subsequent preparation steps by ultrasonication, to remove debris and relic abrasive. Sections were

111 thinned to the required thickness with SiC 800-1200 powder, then on bonded diamond laps, and

112 finalized with diamond paste down to 0.25 μm. Polished sections were studied using polarizing optical

113 microscopy with magnifications ranging from 35-400×. Locations without visible mineral inclusions

114 and/or underlying grains were pre-selected for later electron probe microanalysis. Most minerals in the

115 studied samples were too small for optical identification and were identified by EPMA.

116 **Scanning electron microscopy - SEM**

117   The surfaces of etched and unetched fractures freshly produced in the laboratory were imaged by

118 SEM. Specimens were vapor-etched over 40 vol% HF solution for 20 s and dried afterwards. Stub-

119 mounted etched and unetched specimens were sputter-coated with ~15 nm W. Secondary electron

120 images were obtained in a Zeiss Supra 40 VP Ultra SEM instrument, operated at 10^{-3} Pa vacuum

121 chamber pressure, acceleration voltage 10 kV at a beam current of 10 nA. With current settings,

122 instrument resolution was about 2 nm, whereas opal sphere diameters range from ~100-600 nm. For

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123 each specimen, observed spheres were traced manually before being processed digitally with ImageJ

124 software (Abràmoff et al. 2004). Average sphere diameters were calculated from the computerized data

125 of four-hundred particles.

126 **Electron probe microanalysis - EPMA**

127 Polished thin sections were prepared for analysis by sputter coating with ~20 nm carbon to prevent

128 charging. Quantitative element concentrations were determined using a JEOL JXA 8200 Superprobe.

129 Chamber vacuum was at 3×10^{-2} Pa or better. The instrument was operated at 15 kV acceleration voltage

130 and 20 nA beam current (on Faraday cup). During measurements, the beam diameter at the point of

131 incidence was focused to 1 μm. We measured opal compositions at different beam diameters (1-20 μm),

132 15 kV, and 20 nA, in 10 spots randomly distributed over some specimens to assess the effect of areal

133 current density on element migration (especially Na) and measurement validity. Compositions obtained

134 at these conditions did not vary systematically or significantly, showing that EPMA at small beam

135 diameters should be applicable to analyze opal, but is obviously limited by the respective lower limit of

136 detection (LLD) of the measured elements. Automated and manual measurements of opals were

137 alternated with measurements of internal standard reference materials (e.g., feldspar, quartz) to identify

138 systematic errors. At least one-hundred point analyses were acquired from each opal specimen.

139 Acquisition time for each Na analysis was set to 5 s on peak and 5 s on background. Peak and

140 background of other elements were measured for 10 s each. X-ray signal was recorded on five WDS

141 detectors (LIFH, PETH, PETJ, 2×TAP). Sodium and potassium were both allocated to a separate WDS

142 detector. Sodium and aluminum were counted first, while silicon and potassium were counted in the

143 second run, as suggested by Morgan and London (2005). The instrument was internally calibrated

144 using synthetic/natural silicate, oxide, sulfate, and REE-phosphate standards. During measurements,

145 the acceleration voltage and beam current were identical to the standardization conditions for all

146 elements. With the above analytical setup, resulting net lower limits of detection were at around

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147   0.01 wt% for most elements, but around 0.03 wt% for Na_2O. Raw data were corrected using the ZAF

148   algorithm and are presented as element oxides, notably Na_2O, K_2O, MgO, CaO, SrO, BaO, MnO,

149   Al_2O_3, Fe_2O_3-total, TiO_2, and SiO_2. Given its abundance, absolute analytical error for SiO_2 is around

150   0.50 wt%. Water contents were calculated as the difference between the measured total and 100.00

151   wt%. These values are directly influenced by the analytical errors in the element species actually

152   measured. Repeated analyses of opals over a 3.5-year period revealed no increase of the measured total.

153   Therefore, desiccation of the specimens in SEM/EPMA vacuum seems negligible. Elemental maps

154   were made using the WDS detectors. Operating conditions were 15 kV accelerating voltage and 20 nA

155   beam current (on Faraday cup), with a beam diameter of 1 μm and 60 ms counting time per 0.5-1 μm

156   pixel size.

157   **X-ray powder diffraction - XRPD**

158   A number of sub-samples were prepared from counterparts of thin-sectioned material, hand-picked

159   under a stereo microscope and pre-crushed in an agate mortar to pass a 325-mesh (44 μm openings)

160   sieve. About 5 g of pre-crushed material was then charged into a ball mill equipped with a stainless

161   hardened steel ball and ground under acetone for 10 min at low rotor speeds to an average particle size

162   of approximately 5 to 20 μm. The slurry was poured out into a Petri dish and the grinding jar rinsed

163   with acetone to transfer all material. Specimens were covered and allowed to dry overnight in an oven

164   at 35 °C, after which the dried powder was homogenized and stored in a polyethylene vial. For X-ray

165   analysis, about 0.5 g of prepared powder was mounted in a specimen holder by side-loading to

166   minimize preferred orientation. For specimens containing quartz, the position of the (101) peak was

167   used as an internal standard. Opals and the quartz-free Yowah samples were measured in an aluminum

168   specimen holder (a=4.0496 Å) so that the diffractograms could be calibrated. Diffractograms were

169   recorded 6-65 °2θ on a PDF-2 X-ray instrument from EFG GmbH Berlin operated at 40 kV and 20 mA,

170   producing non-monochromated Ni-filtered CuKα radiation with λ=1.541718 Å. Step size was set to

171 0.04 °2θ at 4 s acquisition time per step. Modal mineral contents were determined from full-profile

172 analysis using the Match 1.11f software package (Crystal Impact GbR, Bonn, Germany). Lower

173 detection limits were ~1-2 vol%.

174

175 **RESULTS**

176 **Petrographic description of silicified samples**

177 The silicified sediments from Andamooka investigated here consist of silty mudstones,

178 conglomerates, an opal breccia, and a silicified pebble. Opal-replaced materials include gray and

179 translucent white mollusc shell pseudomorphs, and coniferous wood. A friable coating of

180 unconsolidated mud on the surface indicates selective silicification. The majority of opal-bearing

181 sediments are intensely opal-cemented, resulting in a very low porosity of the consolidated product.

182 Opal-cemented, silty mudstones contain some light brown to gray, well-rounded, flat or elongate

183 argillaceous siltstone and shale lithoclasts up to 8 mm long in an almost white to light grayish-brown

184 matrix. The matrix mainly consists of kaolinite books, detrital sub-rounded quartz, and minor lath-like

185 illite. Light brownish opal-A partially replaced the clay matrix without preserving original structures.

186 Colorless and transparent honey-colored opal-A intrudes the matrix and light brownish opal and is

187 parallel to subparallel to the primary bedding direction (Fig. 2a).

188 Opal-cemented conglomerates consist of light gray to brown, poorly sorted, well-rounded,

189 elongated quartz-arenite and quartzite lithoclasts up to 20 mm long in a pale red to gray kaolinitic

190 matrix with sand-sized, sub-rounded to well rounded quartz, and trace amounts of illite. The grain-

191 supported microquartz-cemented opal breccia contains highly angular, 2-40 mm large, light yellow and

192 brown clasts with abundant weakly birefringent domains and occasional veins of transparent opal-A

193 with intense play-of-color (POC). Clast surfaces are often covered by water-clear botryoidal amorphous

194 silica. X-ray diffraction patterns of whole rock samples indicate a mixture of quartz and opal-CT (see

195 XRPD section). Weakly birefringent domains inside the clasts contain some chalcedony. Some of the

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196   clasts also contain concentrically zoned, round to ellipsoidal ooid structures that rarely exceed 300 μm

197   in size. The ooids are deformed when in contact with authigenic K-feldspar grains. Another sample rich

198   in microstructural features is the gray, ~60 mm large, silicified pebble (Table 1). It is composed of

199   quartz, traces of transparent to translucent hydrous silica phases, and very few, minute-sized (2-10 μm)

200   illite and barite grains. Some rounded pores contain transparent opal-A with intense blue to green POC.

201   Rhombohedral pseudomorphs are widespread in this sample and consist of euhedral quartz grains

202   ranging from 10-30 μm in size. The pseudomorphs contain small cavities frequently lined with

203   translucent white, weakly birefringent, botryoidal aggregates <20 μm across (Fig. 2b). Coniferous

204   wood with well-preserved tracheids and bordered pits consists of white to light brownish common

205   opal-A. Veins developed perpendicular to the rays are filled with colorless to transparent honey-colored

206   opal-A and occasionally contain loose fragments with tracheid structures. Mollusc shell pseudomorphs

207   consist of either translucent white or gray opal-A with a vivid blue to red POC.

208   Spherical, concentric zoned, dark-brown limonite concretions from Yowah range from 2-8 cm

209   across. Whole rock XRPD analyses reveal the abundant presence of goethite and to a minor extent

210   hematite, kaolinite, and illite. Dark-brown goethite/hematite layers alternate irregularly with light-

211   brown clay mineral layers and opal-A veins. The clay mineral bands, that are tens to hundreds of

212   micrometers wide, coat the surface of voids and are composed of kaolinite, illite, anatase, and a number

213   of aluminum-phosphate-sulfate (APS) minerals. Opal-A fills pseudomorphs after rhombic elongated

214   minerals - possibly gypsum or feldspar - and the network of thin concentric and radial fractures inside

215   the ironstone nodules. Opal-A in veins is transparent and predominantly displays a strong POC that

216   spans the entire visible spectrum. A fine parallel striation in vein opals is common among the Yowah

217   samples and infrequently extends into the narrow vein ends. The rhombic pseudomorphs (Fig. 2c),

218   frequently up to 1.5 mm long with cracks (<20 μm) developed perpendicular to the longest axis, often

219   form aggregates and fan-like arrangements in the goethite groundmass. They contain transparent

220   opal-A with an intense violet-blue POC.

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221   Generally, opal-A fills millimeter to centimeter wide voids and cracks in silicified sediments.

222   Precious opals have a gray, colorless transparent or rarely translucent white body color. Common opals

223   are white, light brown, colorless, or transparent honey-colored. Colorless and transparent honey-

224   colored opals usually do not display a POC except for a few scattered millimeter-sized faint violet to

225   blue domains. Some common opals therefore resemble low-quality precious opal-A. Precious and

226   common opals frequently display <30 µm wide, polygonal desiccation cracks (Fig. 2d). The cracks in

227   precious opals remain open, while those in white and light brown common opals often contain

228   authigenic illite, kaolinite, and occasionally some minute-sized (hundred nanometer) barite, anatase, or

229   gypsum crystallites. Neither cracks nor inclusions are visible with the unaided eye in hand-specimen. In

230   many samples, we observed that large cracks (>50 µm) and millimeter-long faults in white to light

231   brown common opal are filled with colorless or transparent honey-colored opal-A, which sporadically

232   displays a faint violet POC.

233   **The Andamooka host rock and opal-associated minerals**

234   The unsilicified friable host rock at Andamooka is an extensively bleached, white to light-yellow,

235   iron stained mudstone without evidence of bedding. X-ray diffraction analyses of whole rock samples

236   reveal a modal mineral content (in vol%) of about 50% kaolinite, 35% quartz, 10% alunite, and minor

237   amounts of illite, hematite, anatase, and barite, which is consistent with optical inspection of thin

238   sections and X-ray mapping. The rock predominantly consists of kaolinite particles <2 µm,

239   homogeneously distributed kaolinite books, and silt-sized intense corroded quartz grains (Fig. 3a). This

240   rock is characterized by large (up to 200 µm) randomly distributed pockets throughout the sediment.

241   These are filled with colorless, micrometer-sized, pseudocubic alunite crystals. In the clay matrix,

242   kaolinite particles (<2 µm) are closely associated and replaced by alunite crystals up to 5 µm.

243   The main minerals in silicified samples from Andamooka are kaolinite and quartz. Kaolinite

244   usually occurs as a fine-grained, gray to brown mass composed of clay-sized particles. Throughout the

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245 kaolinitic groundmass, rare vermicular kaolinite books and lath-like illite particles are scattered

246 irregularly. Blocky kaolinite aggregates can reach a size of 200 μm, whereas illite particles are often

247 <20 μm and rarely exceed 100 μm in size. Replacement of illite by kaolinite is widespread and appears

248 in the form of up to 10 μm thick kaolinitized lamellae parallel to the direction of elongation (Fig. 3b).

249 Microprobe analyses and X-ray mappings of clay-rich areas indicate that considerable amounts of

250 xenomorphic anatase, barite, and hematite grains <5 μm are present as impurities. Detrital quartz grains

251 are commonly sub-angular to rounded and intensely fractured. Authigenic quartz frequently displays

252 corrosion pitting covered by botryoidal amorphous silica. In places, zoned, intensely corroded, tabular

253 barite grains (<100 μm) are accumulated on the surface of fracture-coating botryoidal silica. Gypsum

254 particles (<2 μm) with granular appearances are developed exclusively in cracks within opal-A.

255   Pores in silicified sediments contain alunite crystals that are predominantly smaller (<3 μm) than

256 those in the host rock. The alunite-containing pores are often surrounded by transparent opal-A. Where

257 present, alunite normally occurs in association with clay-sized kaolinite particles, and occasionally with

258 barite and K-feldspar. Euhedral, elongated K-feldspar crystals occur as transparent grains <200 μm in

259 size, some of which have prominent parallel dissolution channels along the c-axis (Fig. 3c). Pores filled

260 with K-feldspar may contain barite in the form of euhedral tabular grains and concretionary masses. In

261 one sample, it was observed that several pores contained partially dissolved K-feldspar and massive

262 barite with embedded pseudocubic alunite. Chalcedony is a trace constituent within breccia clasts, and

263 is virtually absent from other samples. In rock thin sections chalcedony occurs as translucent white,

264 length-fast, spherulitic and rarely as a wall-lining filling of isolated pores and veins <200 μm.

265 Gorceixite and members of the gorceixite-florencite-(Ce) solid-solution series have been identified by

266 EPMA as very rare, minor constituent in the opal breccia from Andamooka. Gorceixite occurs in

267 euhedral, up to 50 μm large, transparent crystals. Gorceixite-florencite-(Ce) forms ~30 μm thick rims

268 lining pores left by grain dissolution. The rims display a patchy and broad growth zonation when

269 viewed under backscattered electron (BSE) imaging (Fig. 3d). Submicrometer-sized APS crystals in

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270   this sample occur in clay-rich bands lining detrital quartz surfaces. Goethite in the Yowah rock samples

271   typically forms aggregates (<4 µm) of acicular crystals, with blackish to reddish brown color in thin

272   section. Less frequently, reniform aggregates with radial structure line opal-filled veins. APS minerals

273   in the Yowah samples often are stubby six-sided, <3 µm large grains confined to clay layers.

274   **SEM observations on opals**

275   Opal-A from both sample localities consists of spheres with variable size, ordering, internal

276   structure, and degree of cementation (Fig. 4a-d). Figure 5 shows that spheres of different diameter are

277   grouped into monodisperse or polydisperse ones. Colorless and transparent honey-colored common

278   opals as well as transparent, translucent white, and gray precious opals consist of regularly arranged

279   monodisperse spheres. The average diameter of monodisperse spheres ranges from 140-290 nm with a

280   relative standard deviation (RSD) between 3.8-6.0%. White and light brown common opals consist of

281   irregularly arranged, polydisperse, round to ellipsoidal spheres with an average diameter of 160-

282   320 nm and a RSD between 10.6 and 15.6%. A smooth thin layer of silica often coats coalesced

283   spheres. Mollusc shell pseudomorphs consist of well-ordered monodisperse spheres with an average

284   diameter of 210-260 nm. In part, deformation of one shell sample resulted in hexagonal sphere cross-

285   sections. Deformed, elongated to ellipsoidal spheres in the Yowah samples often display up to three

286   unfilled cores. The deformed spheres occur in <5 µm wide veins and along the surface of >100 µm

287   wide goethite-lined veins filled with uniformly sized spheres. The degree of sphere deformation in wide

288   veins increases from the vein interior towards the goethite margin. After HF etching, spheres in void-

289   filling common and precious opals often display a central 20-50 nm-sized nucleus or central depression

290   surrounded by up to two concentric shells. Opals differ by the degree to which the interstices between

291   spheres are filled with silica cement. For example, spheres in mollusc shell pseudomorphs with a vivid

292   POC contain considerably less cement than those in void-filling opals without a POC. This feature is

293   especially pronounced in unetched specimens.

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294   Morphological changes of opaline phases inside partly dissolved rhombohedral pseudomorphs in

295   the silicified pebble were captured by SEM images (Fig. 4e, f). These revealed micro- to nano-sized

296   particle changes within a distance of a few hundred micrometers. Each pore coating in the

297   pseudomorphs contains silica particles of individual size and morphology. The particles are in direct

298   contact with the underlying quartz substrate and have a microstructure of interpenetrating blades

299   similar to those observed in siliceous sinter modified by progressive diagenetic overprint (Lynne et al.

300   2005). We observed two textural features that have been described as poorly bladed and well-bladed

301   opal-CT lepispheres (Flörke et al. 1976). Well-bladed lepispheres are either round, up to 1.8 µm across,

302   and consist of well defined ~50 nm thick blades with smooth edges, or form cauliflower-like

303   aggregates of coalescent lepispheres (5 to over 20 µm across) with ~60 nm thick platelets and jagged

304   edges. Poorly bladed lepispheres are ellipsoidal, up to 1.5 µm large aggregates of ~120 nm thick

305   platelets with jagged edges. The jagged edges of lepisphere platelets resemble aligned 60-120 nm large

306   silica nanospheres.

307   **EPMA analysis of opals and associated minerals**

308   Impurities of all opal-A samples are Al_2O_3, Fe_2O_3, CaO, Na_2O, K_2O, MgO, and BaO. All

309   impurities but Al_2O_3 and CaO appear in trace amounts <0.1 wt%. A typical location for electron probe

310   microanalysis on polished thin sections is shown in Figure 6. Representative analyses of opals are

311   presented in Table 2. Water contents (H_2O + OH), calculated by balance with 100.00 wt%, range

312   between 4.00 and 8.20 wt%. The sum of cation impurities does not exceed 2.39 wt% and in most cases

313   is below 1.45 wt%. No co-variation is observed between the total impurity level and the visual

314   appearance of opals. Sodium and potassium account for less than 20% of the impurity concentration.

315   SrO, MgO, MnO, and TiO_2 contents are generally low (<LLD to 0.03 wt%) and do not vary

316   systematically. While BaO contents mostly range from 0.01-0.03 wt%, relative BaO enrichment (0.07-

317   0.09 wt%) is observed in void-filling white and transparent opal of one conglomerate sample. It is

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318   evident that the Al content between adjacent common/precious and different-colored common opals

319   does not vary significantly (<10%). Significant variations in Al and Ca content are recorded between

320   void-filling opals (0.75-1.21 wt% Al_2O_3; 0.04-0.11 wt% CaO) and mollusc shell pseudomorphs (1.31-

321   1.53 wt% Al_2O_3; 0.27-0.40 wt% CaO). Fe_2O_3 is less abundant in Andamooka opal (up to 60% less)

322   than in Yowah vein opal. Yowah opal-A in rhombic pseudomorphs and veins shows similar trace

323   element profiles. Only Fe_2O_3 varies significantly from about 0.03 wt% in the pseudomorphs to

324   0.21 wt% in veins.

325   The main difference in the geochemical characteristics of all studied opals is their Na/K ratio.

326   From Figure 7, it is evident that the sphere size distribution of opal-A in voids and pseudomorphs

327   varies with the Na/K ratio. Monodisperse spheres display a narrow range of values <1.2, while

328   polydisperse spheres have variable ratios >3.0. In contrast to Na/K, the sum of Na and K, which is

329   0.07 wt% on average, allows no distinction between spheres of different size distribution. The Na + K

330   of monodisperse spheres scatters from 0.03 to 0.13 wt%, while polydisperse ones have concentrations

331   from 0.05 to 0.12 wt%.

332   Several minerals are associated with opal-A such as kaolinite, illite, and K-feldspar. Their

333   compositions are collated in Table 3. Microprobe data show that the illite from both deposits is

334   predominantly a K-rich variety, low in Mg and Fe. The chemical composition of kaolinite and illite

335   remains uniform throughout each rock sample but varies slightly between Andamooka and Yowah

336   samples. The relatively iron-enriched opals from the Yowah samples coexist with kaolinite and illite

337   that contain ~50 and ~80% more Fe_2O_3 respectively. The goethite formed in Yowah ironstone nodules

338   has an average Al substitution of <3 mol% estimated from the position of the 110 (4.185 Å), 111

339   (2.449 Å), and 130 (2.697 Å) diffraction lines (Fitzpatrick and Schwertmann 1982; Schulze 1984). This

340   value agrees well with EPMA data that indicate an average Al substitution of ~1.6 mol%. Based upon

341   probe analyses, K-feldspar compositions range from Or_{91} to Or_{99} in the Andamooka samples and from

342   Or_{92} to Or_{95} in the Yowah samples.

14

343   APS minerals (for review see Dill 2001) have been identified in silicified sediments and the

344   Andamooka host rock. The unit-cell dimensions a (6.98 Å) and c (17.32 Å), calculated from XRPD

345   measurements, indicate that alunite in the Andamooka host rock is a K-rich member of the

346   alunite/natroalunite solid-solution series (compared to peak positions from Parker 1962). EPMA

347   analysis shows that alunite in the Andamooka host rock has a molar K/Na >13, whereas silicified rocks

348   contain alunite with a molar K/Na of 5-9. The amount of BaO in the host rock alunite is considerably

349   lower than in alunite from silicified sediments (0.13 and 3.64 wt% respectively). Conversely, alunite in

350   the host rock contains more K_2O than alunite in silicified sediments (10.13 and 7.94 wt% respectively).

351   Other APS minerals identified in an Andamooka sample are gorceixite and members of the

352   gorceixite-florencite-(Ce) solid-solution series. Gorceixite crystals have homogenous compositions and

353   show minor substitution of Ba by Ca and Ce, with a molar Ba/(Ca + Ce) >6.2. Gorceixite-florencite-

354   (Ce) crystals display compositional zoning because of Ba-Ce substitution. Their molar Ba/LREE is

355   >1.5, with up to 9.07 wt% $LREE_2O_3$ (sum of La, Ce, Pr, and Nd oxides). APS minerals from the Yowah

356   field have heterogeneous and complex compositions, with variable amounts of K, Sr, Ba, and Ca. The

357   APS minerals might be described as potassian goyazite, but their composition could only be obtained

358   from <3 μm large crystals, making it difficult to provide an accurate classification. The molar P/S ratio

359   of APS minerals (except alunite) from Andamooka is >25, while those from Yowah have a ratio <2.

360   The molar Al/Fe^{3+} of these minerals from Andamooka is >15, while those from Yowah have a ratio <4.

361   **Opal X-ray diffraction data**

362   The typical XRPD patterns of opal phases in the samples studied are shown in Figure 8.

363   Diffractograms of opal-A are characterized by a major broad asymmetric reflection located at 4.004 Å

364   (22.2 °2θ) on average. The position of the main peak varies from 3.995 to 4.015 Å (22.25 to 22.14 °2θ)

365   between individual samples. The full width at half maximum (FWHM) of this peak ranges from

366   6.75-7.51 °2θ. An additional very broad reflection of low intensity with a maximum at 1.95-2.01 Å

15

367 (46.54-45.06 °2θ) is observed in about half of the diffractograms. We found no co-variation between

368 peak shape/position and the visual appearance, micromorphology, or chemical aspects of opal-A. The

369 XRPD pattern of the opal breccia shows characteristic quartz peaks and a prominent reflection centered

370 at 4.101 Å (21.67 °2θ) with a FWHM of 0.96 °2θ and a slight shoulder on the high-°2θ side. The

371 position of this peak corresponds most closely to the d-value of α-tridymite *hkl* (-404) (Flörke 1955) at

372 4.107 Å (21.6 °2θ). An additional peak of lower intensity is located at ~2.50 Å (35.94 °2θ). According

373 to the Jones and Segnit (1971) classification scheme the peak shapes/positions are consistent with

374 opal-CT. The diffractogram lacks additional cristobalite-related peaks (e.g., Ghisoli et al. 2010)

375 between 3.14 Å (28.5 °2θ) and 2.84 Å (31.5 °2θ). A minor contribution of opal-A to the diffraction

376 pattern cannot be excluded.

377

378 **DISCUSSION**

379 **Geochemical features of opal-A**

380 Petrographic and mineralogical analyses indicate that opal-A is the main silica phase in the

381 silicified sediments from Andamooka and Yowah. Microprobe analyses of 20 opals yielded data for 10

382 cation impurities in amorphous silica spheres. The results show that the composition of common and

383 precious opal-A is highly variable. Seemingly, opalized mollusc shell pseudomorphs partially preserved

384 the Ca-rich composition of the parent material. Yowah opal composition data are absent from literature,

385 but to our knowledge there are three chemistry studies on void-filling opal-A clearly assigned to the

386 Andamooka opal field (Bayliss and Males 1965; Brown et al. 2004; Gaillou et al 2008a) to which we

387 can compare our data. However, some literature data lacks relevant elements such as K and Ba (Bayliss

388 and Males 1965) and Ba (Brown et al. 2004). The majority of Andamooka opal in the present study

389 contains fewer impurities, specifically K, Ca, and Al, than those mentioned in the literature.

390 Compositional variations may arise from the amount of water and additional substitution of Si^{4+} by Al^{3+}

391 or Fe^{3+}, which is compensated by the incorporation of mono- and divalent cations and OH groups

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392   (Webb and Finlayson 1987; Gaillou et al. 2008a). The positive correlation between the sum of trivalent

393   cations (Al^{3+}, Fe^{3+}) and mono- and divalent cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) in Andamooka and

394   Yowah opal-A illustrates such a relationship (Fig. 9). This relation indicates that cations are structurally

395   incorporated into growing spheres and do not accumulate solely on the particle surface.

396   Some authors noted that precious opal-A has a more constant impurity concentration than common

397   opal-A (e.g., Gaillou et al. 2008a). In contrast, others reported that precious and common opals show

398   very similar trace element profiles (Bayliss and Males 1965; McOrist and Smallwood 1997; Brown et

399   al. 2004). Our results do not reveal a relation between the sum of impurities and the opal-A variety. In

400   fact, opals composed of monodisperse spheres, regardless of their gemological classification, tend to

401   have less constant element concentrations than opals composed of polydisperse spheres. This result

402   cautions against the gemological distinction between common and precious opal as a primary

403   determinative tool.

404   Compositional variations could also be related to microscopic structures observed in opal-A. Thin

405   section petrographic analysis revealed that <30 μm wide cracks in white and light brown common

406   opal-A often contain illite, kaolinite, barite, anatase or gypsum. Clay-related elements such as Na, K,

407   Ca, Mg, and Al also represent the major opal impurities. Slight admixture of mineral impurities in

408   cracks may shift the measured cation content of bulk opal samples towards higher values, hardly

409   recognizable by comparison of mono- and polyvalent cations. These impurities represent a significant

410   factor for composition-based interpretations. Therefore, caution must be exercised when analyzing bulk

411   samples because subtle but significant mineral inclusions may be overlooked.

412   **Relation between the opal-A Na/K ratio and silica sphere properties**

413   We have identified that monodisperse and polydisperse spheres in Andamooka and Yowah opal are

414   separated by their Na/K ratio, restricting the appearance of monodisperse spheres to values <1.2 and

415   polydisperse spheres to values >3.0. Interestingly, this relation includes void-filling opal-A and

17

416   pseudomorphs, which most likely formed by different mechanisms. Other trace elements do not appear

417   to correlate with the silica sphere micromorphology in the present study. This relation is surprising,

418   considering the low concentration of monovalent cations. Some researchers suggest that polydisperse

419   spheres sediment from thicker, more concentrated solutions than monodisperse spheres (e.g., Darragh

420   et al. 1966; Gaillou et al. 2008b). Accordingly, slow sphere growth and sedimentation are considered a

421   prerequisite for precious opal formation. Spheres can grow by aggregation of subparticles, as indicated

422   by SEM observations on natural opal-A (Darragh et al. 1966; Gaillou et al. 2008b) and experiments

423   (e.g., Conrad et al. 2007). Electrolytes increase the polymerization of silica in solution and accelerate

424   the aggregation and subsequent sedimentation of silica spheres. K reduces the repulsive interparticle

425   forces more effectively than Na (Sonnefeld et al. 1995; Dove and Craven 2005), which suggests that

426   unstable, polydisperse spheres could have a low Na/K fingerprint. This contrasts with our observation

427   of monodisperse spheres with a lower Na/K ratio than polydisperse spheres.

428   Although monovalent cations modify the solubility and surface properties of amorphous silica,

429   polyvalent cations are more efficient at reducing the amorphous silica solubility and screening length of

430   the electrical double-layer around charged silica particles (e.g., Marshall and Warakomski 1980;

431   Wijnen et al. 1993; Dove and Craven 2005). Deduction of opal formation mechanisms from its

432   monovalent cation fingerprint alone seems insufficient, as polyvalent cations, anions, and pH may play

433   a more significant role in silica colloid behavior. Based on these considerations, it appears unlikely that

434   Na and K control sphere size distribution, despite the correlation of Na/K ratio and dispersity. The

435   absence of this relation implies that other parameters such as pH and salinity, which cannot be derived

436   directly from the opal composition, may play a more important role in opal formation.

437   **Opal-associated minerals - implications for opal-forming solutions**

438   We suggest that the Na/K ratio represents significant differences in the overall solution

439   characteristics. The spatial, and therefore temporal, relation of opal with monodisperse spheres

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440   intruding opal with polydisperse spheres illustrates this major change. It is important to note that the

441   opposite case was never observed. The high Na/K of polydisperse spheres may mark a solution

442   composition triggered by hydrolysis of Na-rich minerals. The absence of such minerals from the

443   samples and the low Na/K of uniform spheres could imply that there was sodium removal from

444   solution. Alternatively, sodium phases could have been unstable in the opal-bearing rocks. The solution

445   composition changed after the precipitation of polydisperse spheres, along with deformation and

446   cracking probably induced by dehydration or small-scale faulting. Such dehydration events are

447   consistent with a fluctuating groundwater table due to an arid climate, which is considered essential for

448   opal formation at the Australian fields (Darragh et al. 1966; Senior et al. 1977; Barnes et al. 1992).

449   Silica liberation at opal fields is commonly attributed to the kaolinitization of feldspar, mica, and clay

450   minerals at neutral to acidic pH. These reactions provide K^+ and Ba^{2+}, components that are essential for

451   the authigenesis of alunite, illite, barite, or gorceixite. An alternative path to potassium liberation could

452   be alunite weathering at increasing pH. In this case, another source provides silica in sufficient

453   quantities for opal precipitation. This seems unlikely because illite and K-feldspar formation, at the

454   expense of alunite, remove silica from solution.

455   The association of alunite, kaolinite, illite, and K-feldspar might serve as a tracer for the solution

456   composition as it indicates large variations of pH and silica concentration (Raymahashay 1968). The

457   co-occurrence of opal-A with opal-CT, chalcedony, and quartz also suggests that the silica

458   concentration in solution varied significantly. The kaolinite-alunite-opal assemblage is common in

459   Australian opal deposits (Jones et al. 1966; Bird et al. 1990; Barnes et al. 1992) and is reported for

460   weathering profiles associated with the action of acidic sulfurous solutions on clay minerals and mica

461   (McArthur et al. 1991; Blanco et al. 2008; Wray 2011). Extensive replacement of kaolinite by alunite in

462   the Andamooka host rock implies such an acidic environment in which silica is solubilized and leached

463   from the deeply weathered mudstone. Alunite forms at pH <5.5 whenever sufficient quantities of sulfur,

464   potassium and aluminum are available (Raymahashay 1968). Oxidation of the cretaceous dark colored,

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465 pyritic claystone below the opal level (Carr et al. 1979; Alexander et al. 2006) could release necessary

466 sulfur and induce a pH drop. As ferrolysis is the most likely cause of groundwater acidification in

467 inland Australia (McArthur et al. 1991; Thiry et al. 2006), impregnations by iron oxides at Andamooka

468 and the formation of iron concretions at Yowah could be remnants of this process. At 25 °C, the

469 kaolinite-alunite conversion requires a pH ~5 at quartz saturation and ~3.7 at amorphous silica

470 saturation (Raymahashay 1968; Fig. 10a). It is therefore likely that uniform spheres with low Na/K

471 formed during episodes of alunite precipitation at pH <3.7. Bird et al. (1990) measured a K-Ar age of

472 8.4 ± 0.1 Ma obtained from alunite in the Andamooka precious opal field, and concluded that alunite is

473 a late-stage product of Late Miocene weathering. This might indicate that monodisperse spheres with

474 low Na/K are of the same age.

475 **Formation of uniform spheres at proposed acidic pH**

476 Opal-A and alunite can co-precipitate at pH <3.7. This pH region comprises the isoelectric point

477 (IEP) of amorphous silica, where the solubility of amorphous silica and stability of colloidal silica

478 exhibit a local maximum (Fig. 10b). Differences between Na and K cations, with respect to aggregation

479 kinetics, are not to be expected (Wijnen et al. 1993). At the IEP, sphere aggregation is slowed down

480 even at high ionic strengths (Kobayashi et al. 2005). Additionally, experimental work on geothermal

481 brine solutions demonstrated a significant decrease in silica precipitation at pH ~4 compared to pH 7.5-

482 9 (Rothbaum et al. 1979) and pronounced silica nanocolloid stability at low pH regardless of ionic

483 strength (Conrad et al. 2007). These relationships could possibly explain the absence of a correlation

484 between opal type and total impurity level.

485 Numerous authors have pointed to the existence of stable silica colloids at alkaline conditions

486 only, in order to estimate the pH at precious opal formation (e.g., Williams and Crerar 1985; Brown et

487 al. 2004; Rey 2013) based on the relation between pH and silica sol formation given by Iler (1979).

488 However, the complete reference (Iler 1979, p. 366) states that at pH 8-10, sols are only generally

489 stable in the absence of salts. In this context, it should be noted that natural opal-A develops from

20

490   siliceous fluids with a complex ion composition, which are subject to evaporation and probably

491   significant changes of the ionic strength. This salinity relation is an important aspect that needs to be

492   taken critically when synthetic and natural silica colloid formation is compared.

493   In a broader geological picture it is commonly assumed that precious opal precipitation requires a

494   two-step mechanism occurring at all present opal fields in all local environments. The first step

495   involves the dissolution of feldspar, mica, and clay minerals at low pH and the second step involves

496   silica precipitation at high pH. It seems easier to assume co-formation of all major phases near the IEP

497   of silica without calling for coeval regional and local changes in pH in large areas (e.g., Rey 2013). We

498   propose that slow sphere aggregation could proceed at acidic pH, favoring the growth of monodisperse

499   spheres with repulsive forces large enough to keep them separated in solution, and to arrange them in

500   an ordered array prior to the evaporation of interstitial fluids. On the other hand, polydisperse spheres

501   probably formed at conditions associated with higher pH and different anion composition, resulting in

502   lower amorphous silica solubility, unstable nuclei, or fast aggregation due to lower repulsive

503   interparticle forces. The absence of Na-rich minerals from the samples precludes drawing firm

504   conclusions about the formation conditions of opal-A with high Na/K based on the associated mineral

505   assemblage.

506

507   **IMPLICATIONS**

508   While the conditions discussed apply to Andamooka and Yowah opal-A, the formation of stable

509   uniformly sized silica spheres at acidic conditions can probably be generalized to other sedimentary

510   precious opal deposits. In Australia, the major economically important opal fields lie in the Great

511   Artesian Basin and display systematic geological and mineralogical similarities (Barnes et al. 1992;

512   Landgrebe et al. 2013). They all contain silcretes and abundant sulfate minerals such as alunite and

513   gypsum (Jones et al. 1966; Senior et al. 1977; Thiry et al. 2006). Thus, the geochemical signature of

514   opal-A essentially needs to be complemented with that of its host rock and associated minerals, as they

21

515   record the complex history of opal-forming solutions. In order to achieve this goal, it is mandatory to

516   combine a quantitative opal classification, decoupled from gemological properties, with accurate

517   microanalyses able to distinguish between closely spaced opals and to avoid contamination with

518   mineral inclusions.

519   Based on high-resolution measurements of opals and associated minerals combined with colloid-

520   chemical models from materials science, new insights into the formation and evolution of nanocolloidal

521   silica in natural aqueous systems may be generated. The investigation of opal-A micromorphology and

522   -chemistry may also reveal clues for the understanding of structural and chemical reorganization

523   mechanisms behind silica pseudomorphism. Indeed, further detailed studies that include local analysis

524   of mineral chemistry, structure, and association are necessary to restrict the physico-chemical

525   environment in which opal-A forms. Due to the wide distribution of amorphous silica as a weathering

526   product and cementing agent in a variety of geologically important settings on earth´s surface and

527   subsurface, being a potential precursor for crystalline silica, the formation of natural silica spheres

528   awaits elucidation.

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535   **REFERENCES CITED**

536   Abràmoff, M.D., Magalhães, P.J., and Ram, S.J. (2004) Image processing with ImageJ. Biophotonics

537   International, 11, 36–42.

22

538   Alexander, G.B., Heston, W.M., and Iler, R.K. (1954) The solubility of amorphous silica in water.

539   Journal of Physical Chemistry, 58, 453–455.

540   Alexander, E.M., Sansome, A., and Cotton, T.B. (2006) Eromanga Basin - Lithostratigraphy and

541   environments of deposition. In Cotton, T.B., Scardigno, M.F., and Hibburt, J.E., Eds., The Petroleum

542   Geology of South Australia, Vol. 2, p. 148-166. Department of Primary Industries and Resources,

543   Government of South Australia.

544   Barnes, L.C., Townsend, I.J., Robertson, R.S., and Scott, D.C., Eds. (1992) Opal: South Australia's

545   gemstone, 176 p. Handbook No. 5, Department of Mines and Energy, Geological Survey of South

546   Australia.

547   Bayliss, P. and Males, P.A. (1965) The mineralogical similarity of precious and common opal from

548   Australia. Mineralogical Magazine, 35, 429–431.

549   Bird, M.I, Chivas, A.R., and McDougall, I. (1990) An isotopic study of surficial alunite in Australia 2.

550   Potassium-argon geochronology. Chemical Geology, 80, 133–145.

551   Blanco, J.A., Armenteros, I., and Huerta, P. (2008) Silcrete and alunite genesis in alluvial palaeosols

552   (late Cretaceous to early Palaeocene, Duero basin, Spain). Sedimentary Geology, 211, 1–11.

553   Bogush, G.H. and Zukoski, C.V. (1991) Uniform silica particle precipitation: an aggregative growth

554   model. Journal of Colloid and Interface Science, 142, 19–34.

555   Brown, L.D., Ray, A.S., and Thomas, P.S. (2004) Elemental analysis of Australian amorphous banded

556   opals by laser-ablation ICP–MS. Neues Jahrbuch für Mineralogie Monatshefte, 9, 411-424.

557   Carr, S.G., Olliver, J.G., Conor, C.H.H., and Scott, D.C. (1979) Andamooka opal fields: The geology of

558   the precious stones field and the results of the subsidised mining program, 68 p. Report of

559   Investigations 51, Department of Mines and Energy, Geological Survey of South Australia.

23

560   Conrad, C.F., Icopini, G.A., Yasuhara, H., Bandstra, J.Z., Brantley, S.L., and Heaney, P.J. (2007)

561   Modeling the kinetics of silica nanocolloid formation and precipitation in geologically relevant aqueous

562   solutions. Geochimica et Cosmochimica Acta, 71, 531–542.

563   Crerar, D.A., Axtmann, E.V., and Axtmann, R.C. (1981) Growth and ripening of silica polymers in

564   aqueous solutions. Geochimica et Cosmochimica Acta, 45, 1259–1266.

565   Darragh, P.J, Gaskin, A.J, Terrell, B.C., and Sanders, J.V. (1966) Origin of precious opal. Nature, 209,

566   13–16.

567   Dill, H.G. (2001) The geology of aluminum phosphates and sulphates of the alunite group minerals: a

568   review. Earth-Science Reviews, 53, 35–93.

569   Dove, P.M. and Craven, C.M. (2005) Surface charge density on silica in alkali and alkaline earth

570   chloride electrolyte solutions. Geochimica et Cosmochimica Acta, 69, 4963–4970.

571   Fitzpatrick, R.W. and Schwertmann, U. (1982) Al-substituted goethite - An indicator of pedogenic and

572   other weathering environments in South Africa. Geoderma, 27, 335–347.

573   Flörke, O.W. (1955) Zur Frage des "Hoch"-Cristobalit in Opalen, Bentoniten und Gläsern. Neues

574   Jahrbuch für Mineralogie Monatshefte, 10, 217–224.

575   Flörke, O.W., Hollmann, R., Rad, U.v., and Rösch, H. (1976) Intergrowth and twinning in opal-CT

576   lepispheres. Contributions to Mineralogy and Petrology, 58, 235–242.

577   Gaillou, E., Delaunay, A, Rondeau, B., Bouhnik-le-Coz, M., Fritsch, E., Cornen, G., and Monnier, C.

578   (2008a) The geochemistry of gem opals as evidence of their origin. Ore Geology Reviews, 34, 113–

579   126.

580   Gaillou, E., Fritsch, E., Aguilar-Reyes, B., Rondeau, B., Post, J., Barreau, A., and Ostroumov, M.

581   (2008b) Common gem opal: An investigation of micro- to nano-structure. American Mineralogist, 93,

582   1865–1873.

24

583   Ghisoli, C., Caucia, F., and Marinoni, L. (2010) XRPD patterns of opals: A brief review and new results

584   from recent studies. Powder Diffraction, 25, 274–282.

585   Icopini, G.A., Brantley, S.L., and Heaney, P.J. (2005) Kinetics of silica oligomerization and nanocolloid

586   formation as a function of pH and ionic strength at 25°C. Geochimica et Cosmochimica Acta, 69, 293-

587   303.

588   Iler, R.K. (1965) Formation of precious opal. Nature, 207, 472–473.

589   Iler, R.K. (1979) The chemistry of silica: Solubility, polymerization, colloid and surface properties, and

590   biochemistry, 866 p. Wiley, New York.

591   Jones, J.B. and Segnit, E.R. (1971) The nature of opal I. Nomenclature and constituent phases. Journal

592   of the Geological Society of Australia, 18, 37–41.

593   Jones, J.B., Sanders, J.V., and Segnit, E.R. (1964) Structure of opal. Nature, 204, 990–991.

594   Jones, J.B., Biddle, J., and Segnit, E.R. (1966) Opal genesis. Nature, 210, 1353–1354.

595   Kobayashi, M., Juillerat, F., Galletto, P., Bowen, P., and Borkovec, M. (2005) Aggregation and

596   charging of colloidal silica particles: effect of particle size. Langmuir, 21, 5761–5769.

597   Landgrebe, T.C.W., Merdith, A., Dutkiewicz, A., and Müller, R.D. (2013) Relationships between

598   palaeogeography and opal occurrence in Australia: A data-mining approach. Computers &

599   Geosciences, 56, 76–82.

600   Lynne, B.Y., Campbell, K.A., Moore, J.N., and Browne, P.R.L. (2005) Diagenesis of 1900-year-old

601   siliceous sinter (opal-A to quartz) at Opal Mound, Roosevelt Hot Springs, Utah, U.S.A. Sedimentary

602   Geology, 179, 249–278.

603   Marshall, W.L. and Warakomski, J.M. (1980) Amorphous silica solubilities-II. Effect of aqueous salt

604   solutions at 25°C. Geochimica et Cosmochimica Acta, 44, 915-924.

25

605   McArthur, J.M., Turner, J.V., and Lyons, W.B. (1991) Hydrochemistry on the Yilgarn Block, Western

606   Australia: Ferrolysis and mineralisation in acidic brines. Geochimica et Cosmochimica Acta, 55, 1273–

607   1288.

608   McOrist, G.D. and Smallwood, A. (1997) Trace elements in precious and common opals using neutron

609   activation analysis. Journal of Radioanalytical and Nuclear Chemistry, 223, 9–15.

610   Morgan, G.B. and London, D. (2005) Effect of current density on the electron microprobe analysis of

611   alkali aluminosilicate glasses. American Mineralogist, 90, 1131-1138.

612   Parker, R.L. (1962) Isomorphous substitution in natural and synthetic alunite. American Mineralogist,

613   47, 127-136.

614   Piret, F. and Su, B.-L. (2008) Effects of pH and ionic strength on the self-assembly of silica colloids to

615   opaline photonic structures. Chemical Physics Letters, 457, 376–380.

616   Raymahashay, B.C. (1968) A geochemical study of rock alteration by hot springs in the Paint Pot Hill

617   area, Yellowstone Park. Geochimica et Cosmochimica Acta, 32, 499–522.

618   Rey, P.F. (2013) Opalisation of the Great Artesian Basin (central Australia): an Australian story with a

619   Martian twist. Australian Journal of Earth Sciences, 60, 291-314.

620   Rothbaum, H., Anderton, B., Harrison, R., Rohde, A., and Slatter, A. (1979) Effect of silica

621   polymerisation and pH on geothermal scaling. Geothermics, 8, 1–20.

622   Sanders, J.V. (1964) Colour of precious opal. Nature, 204, 1151–1153.

623   Schulze, D.G. (1984) The influence of aluminum on iron oxides. VIII. Unit-cell dimensions of Al-

624   substituted goethites and estimation of Al from them. Clays and Clay Minerals, 32, 36–44.

26

625   Senior, B.R., McColl, D.H., Long, B.E., and Whiteley, R.J. (1977) The geology and magnetic

626   characteristics of precious opal deposits, southwest Queensland. BMR Journal of Australian Geology &

627   Geophysics, 2, 241–251.

628   Sonnefeld, J., Göbel, A., and Vogelsberger, W. (1995) Surface charge density on spherical silica

629   particles in aqueous alkali chloride solutions. Part 1. Experimental results. Colloid and Polymer

630   Science, 273, 926–931.

631   Stewart, A.M., Chadderton, L.T., and Senior, B.R. (2010) Self-assembly in the growth of precious opal.

632   Journal of Crystal Growth, 312, 391–396.

633   Thiry, M., Milnes, A.R., Rayot, V., and Simon-CoinÇon, S. (2006) Interpretation of palaeoweathering

634   features and successive silicifications in the Tertiary regolith of Inland Australia. Journal of the

635   Geological Society of London, 163, 723-736.

636   Webb, J.A. and Finlayson, B.L. (1987) Incorporation of Al, Mg, and water in opal-A: Evidence from

637   speleothems. American Mineralogist, 72, 1204–1210.

638   Whitney, D.L. and Evans, B.W. (2010) Abbreviations for names of rock-forming minerals. American

639   Mineralogist, 95, 185–187.

640   Wijnen, P.W.J.G, Beelen, T.P.M., Rummens, K.P.J., and van Santen, R.A. (1993) The role of cations in

641   the formation of aqueous silica gels. Journal of Non-Crystalline Solids, 152, 127–136.

642   Williams, L. and Crerar, D. (1985) Silica diagenesis, II. General mechanisms. Journal of Sedimentary

643   Petrology, 55, 312–321.

644   Wray, R.A.L. (2011) Alunite formation within silica stalactites from the Sydney Region, South-eastern

645   Australia. International Journal of Speleology, 40, 109–116.

646   Xia, Y., Gates, B., Yin, Y., and Lu, Y. (2000) Monodispersed colloidal spheres: old materials with new

647   applications. Advanced Materials, 12, 693–713.

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Figure captions

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649 **Figure 1.** Photographs of raw, unprepared sample materials from Andamooka and an ironstone nodule

650 from Yowah.

651 **Figure 2.** Thin section micrographs of microstructural and texture aspects of silicified samples. **(a)** A

652 kaolinite-quartz band with patches of light brown opal (A) within a silty mudstone from Andamooka.

653 Transparent opal (B) intruded and deformed the clay-rich band and light brown opal. **(b)** Partially

654 dissolved rhombic pseudomorphs in the silicified pebble from Andamooka. The cavity walls are lined

655 with translucent, botryoidal silica aggregates. **(c)** A rhombic opal-A pseudomorph embedded in the

656 goethite groundmass of a Yowah ironstone nodule. **(d)** White opal-A from Andamooka with numerous

657 illite-filled polygonal desiccation cracks.

658 **Figure 3.** BSE images (except c) of mineral associations in the host rock and silicified sediments. **(a)**

659 The deeply weathered Andamooka host rock with alunite (Alu), kaolinite (Kln), and quartz (Qz) in

660 their typical spatial context. **(b)** Kaolinite (dark gray) next to illite (white) with kaolinitized lamellae,

661 surrounded by transparent opal-A within a silty mudstone from Andamooka. **(c)** Photomicrograph of an

662 altered K-feldspar grain (center) in direct contact with deformed ooid-like, concentric particles within

663 the opal breccia from Andamooka. **(d)** A gorceixite-florencite-(Ce) rim lining a pore left by grain-

664 dissolution. The rim is surrounded by transparent opal-A within the opal breccia from Andamooka.

665 Gray level differences are related to Ba - Ce substitution.

666 **Figure 4.** SEM images of characteristic appearances of opal-A (a-d) and opal-CT (e and f) after HF

667 etching (except b and c). Scale bar in all images is 1 μm. **(a)** Transparent opal with blue POC from

668 Andamooka, consisting of uniform, well-ordered spheres. Several spheres show a central

669 20-50 nm-sized nucleus or depression (arrows). **(b)** White opal without POC from Andamooka,

670 composed of intersecting polydisperse spheres coated with a thin layer of silica cement. **(c)** Translucent

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671   white opal replacing a mollusc shell from Andamooka. The deformed, uniform, and well-ordered

672   spheres have a hexagonal shape. **(d)** Elongated spheres in a narrow goethite-lined vein in a Yowah

673   ironstone nodule. Some stretched particles contain open pores (arrows). **(e)** A detailed view of

674   well-bladed lepispheres (~30 μm across) lining a partly dissolved quartz surface in the silicified pebble

675   from Andamooka. The lepispheres consist of intergrown ~60 nm thick platelets with jagged edges that

676   resemble aligned silica spheres. **(f)** Poorly bladed, ellipsoidal lepispheres in a cavity located ~200 μm

677   from (e). The platelets consist of 60-120 nm large silica nanospheres and are notably thicker and

678   shorter than in well-bladed lepispheres.

679   **Figure 5.** Sphere size distribution in opal-A. The relative standard deviation (in %) versus the average

680   sphere diameter (in nm) reveals a division into monodisperse and polydisperse spheres.

681   **Figure 6.** BSE image of a typical location for electron probe microanalysis of white opal-A with

682   desiccation cracks (left) and transparent opal-A (right).

683   **Figure 7.** The sum of Na and K (in wt%) versus the Na/K ratio of polydisperse and monodisperse

684   spheres. Error bars represent ±1σ of measurements.

685   **Figure 8.** Typical diffractograms of opal-A (lower graph) and the opal breccia containing opal-CT

686   (upper graph). Diffractograms are shifted for clarity. All opal-A samples display a characteristic broad

687   reflection at ~22.2 °2θ. Quartz impurities (Qz) in the opal breccia originate from quartz cement

688   between the clasts. The major peaks at ~21.7 and ~35.9 °2θ are indicative of opal-CT.

689   **Figure 9.** The correlation between the sum of mono- and divalent cations (Na + K + Ca + Sr + Ba +

690   Mg + Mn) and trivalent cations (Al + Fe^{3+}) in opal-A from Andamooka and Yowah. Andamooka opal

691   compositions from Bayliss and Males (1965) and Brown et al. (2004) are plotted for comparison. A

692   data point from Gaillou et al. (2008a) is located at ~(1.00; 0.77) but was excluded from the plot for

693   legibility.

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694   **Figure 10. (a)** Stability fields of gibbsite, kaolinite, muscovite, K-feldspar, and natural alunite as a

695   function of pH and silica concentration at ambient conditions (after Raymahashay 1968). **(b)** Effects of

696   pH and salinity on the colloid stability in the amorphous silica-water system (after Iler 1979).

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698   **Tables**

699   **Table 1.** Sample characteristics of silicified sediments, opals, and the unsilicified host rock in this

700   study.

Locality	Sample type	Opal-A type	Opal-A color	Associated minerals identified[a]	
				Major constituents	Accessory constituents
Andamooka	mudstone (host rock)	-	-	Kln, Qz, Alu,	Ill, Hem, Ant, Brt
	silty mudstone	C/P	white, light brown, colorless, transparent honey-colored	Kln, Qz	Ill, Ant, Brt, Hem, Alu, Kfs, Gp
	conglomerate with clay matrix	C/P	white, light brown, colorless, transparent honey-colored	Kln, Qz	Ill, Hem, Ant, Alu, Brt, Kfs, Gp
	opal breccia	C/P	colorless	Opl-CT, Qz	Kln, Ill, Brt, Kfs, Alu, Hem, Ant, Cha, Gp, Gcx, Gcx-Fl
	grey pebble	P	transparent	Qz	Opl-CT, Ill, Brt
	mollusc shells	P	translucent white, grey	-	-
	coniferous wood	C/P	white, colorless, transparent honey-colored	-	Kln, Ant
Yowah	ironstone nodules	P	colorless	Gth, Hem, Kln	Ill, Ant, Kfs, Gz

Notes: a - Mineral abbreviations after Whitney and Evans (2010).

Other abbreviations used: C - common opal; P - precious opal; Cha - chalcedony; Flc - florencite; Gcx - gorceixite; Gz - goyazite.

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702   **Table 2.** Representative chemical analyses of opal-A samples by EPMA (given in wt%).

oxide	Andamooka opal-A			Yowah opal-A	
	poly	mono	shells	mono	pseud
Na_2O	0.13	0.10	0.17	0.09	0.08
K_2O	0.03	0.12	0.15	0.18	0.14
MgO	0.03	0.01	0.03	0.02	0.02
CaO	0.06	0.05	0.40	0.09	0.07
SrO	<LLD	<LLD	<LLD	0.01	<LLD
BaO	0.02	0.03	0.02	0.02	0.02
MnO	0.01	0.01	0.02	0.01	0.01
Fe_2O_3-total	0.12	0.07	0.05	0.21	0.03
Al_2O_3	0.96	0.89	1.53	0.89	0.75
TiO_2	0.02	0.01	0.02	0.01	0.01
SiO_2	93.21	90.90	89.40	92.66	92.54
SUM total	94.59	92.20	91.79	94.19	93.67
SUM impurities	1.38	1.31	2.39	1.52	1.13
calculated values					
$(H_2O + OH)$[a]	5.41	7.80	8.21	5.81	6.33
Na + K	0.06	0.09	0.12	0.11	0.09
Na/K	4.16	0.70	0.98	0.45	0.49

Notes: Abbreviations: poly - polydisperse; mono - monodisperse;

shells - monodisperse spheres in mollusc shells; pseud -

monodisperse spheres in rhombic pseudomorphs.

703   a - Calculated by balance of SUM total with 100 wt%.

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711 **Table 3.** Representative chemical analyses of opal-associated minerals from the Andamooka and

712 Yowah precious opal fields by EPMA (given in wt%).

oxide	Andamooka							Yowah			
	Kln	Ilt	Kfs	Alu host	Alu silic.	Gcx[b]	Gcx-Flc[c]	Kln	Ilt	Kfs	Gz
Na_2O	<LLD	0.63	0.47	0.48	0.77	0.14	0.23	<LLD	0.09	0.82	0.17
K_2O	0.06	6.82	16.14	10.13	7.94	0.12	0.09	0.16	6.15	15.52	4.27
MgO	0.03	1.47	0.01	0.04	0.04	0.02	<LLD	0.11	1.27	<LLD	0.03
CaO	0.07	0.27	0.01	0.09	0.24	0.76	1.51	0.08	1.01	<LLD	1.52
SrO	<LLD	<LLD	<LLD	0.02	0.92	0.69	1.30	<LLD	<LLD	<LLD	6.89
BaO	<LLD	<LLD	0.24	0.13	3.64	23.70	14.39	<LLD	<LLD	0.26	3.61
MnO	0.01	<LLD	0.02	0.03	0.01	0.02	<LLD	<LLD	<LLD	0.02	0.16
Fe_2O_3-total	1.50	2.94	0.03	4.27	3.70	0.84	1.09	2.84	3.65	0.06	11.39
Al_2O_3	37.81	29.21	18.26	33.43	33.24	29.88	30.23	37.13	28.86	18.20	26.16
TiO_2	0.02	0.29	0.02	<LLD	0.02	0.04	0.03	0.04	0.09	0.03	0.05
SiO_2	46.65	50.34	64.68	0.19	1.11	0.88	0.29	45.93	52.50	64.34	0.87
P_2O_5	<LLD	<LLD	<LLD	0.32	1.91	26.60	28.16	<LLD	<LLD	<LLD	19.40
SO_3	<LLD	<LLD	<LLD	37.87	33.62	0.89	0.71	<LLD	<LLD	<LLD	11.53
$LREE_2O_3$[a]	<LLD	<LLD	<LLD	<LLD	0.13	2.63	9.06	<LLD	<LLD	<LLD	0.10
SUM total	86.13	91.96	99.86	86.99	87.26	87.21	87.08	86.29	93.61	99.24	86.13

Notes: Alunite in the non-silicified host rock is labeled "Alu host". Alunite in silicified sediments is labeled "Alu silic.".

a - $LREE_2O_3$ is the sum of La, Ce, Pr, and Nd oxides.

b - $LREE_2O_3$ in Gcx (in wt%): La_2O_3 0.21, Ce_2O_3 1.86, Pr_2O_3 0.10, and Nd_2O_3 0.46.

713 c - $LREE_2O_3$ in Gcx-Flc (in wt%): La_2O_3 0.46, Ce_2O_3 7.35, Pr_2O_3 0.23, and Nd_2O_3 1.02.
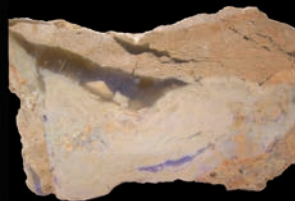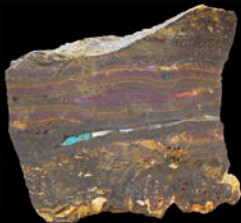
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Figure 1

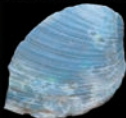conglomerate
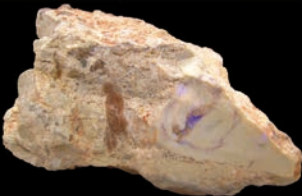
opal breccia

silty mudstone

ironstone nodule

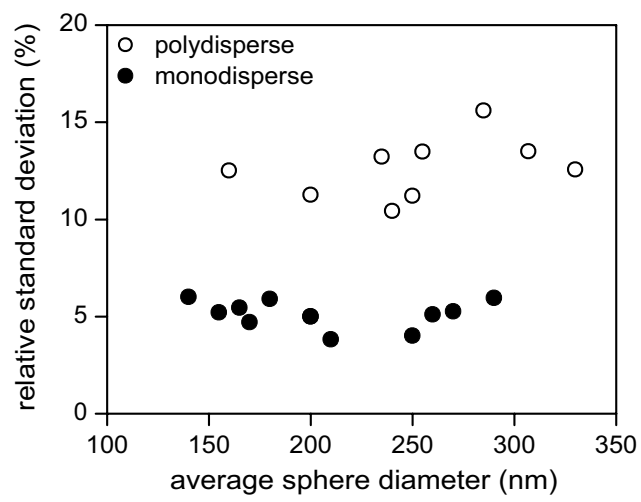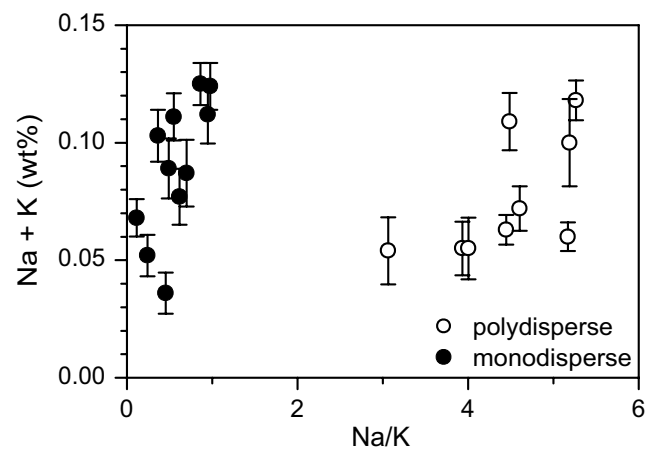coniferous wood

mollusc shell

1 cm

Figure 2
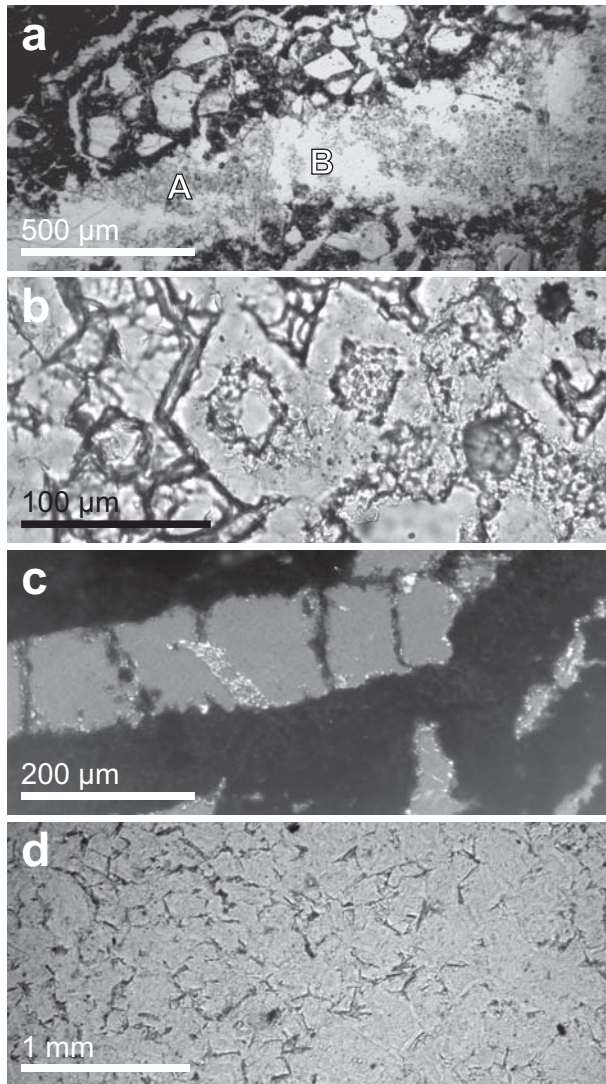
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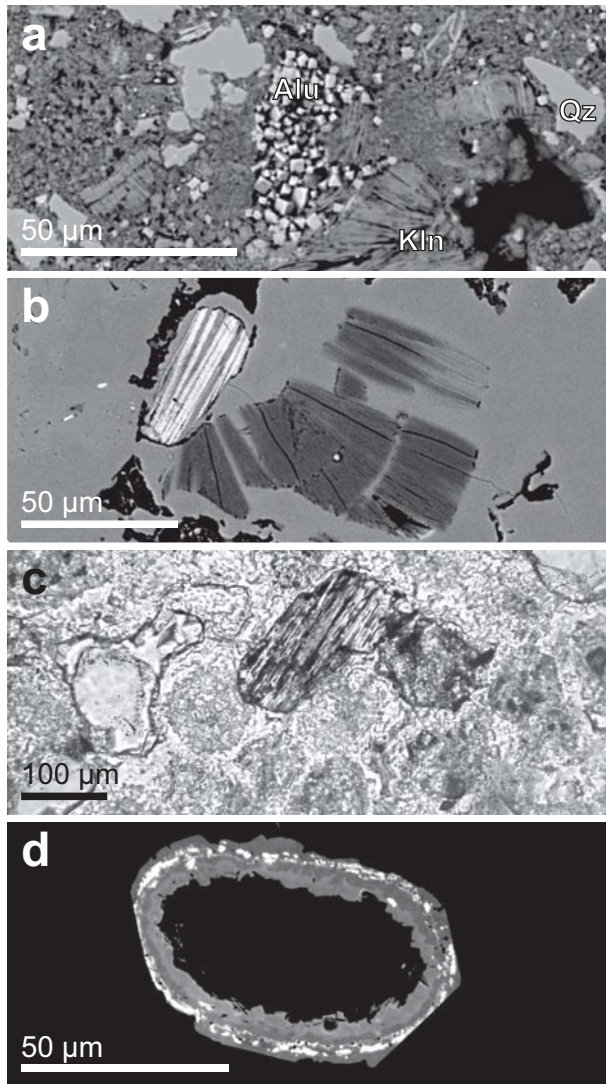
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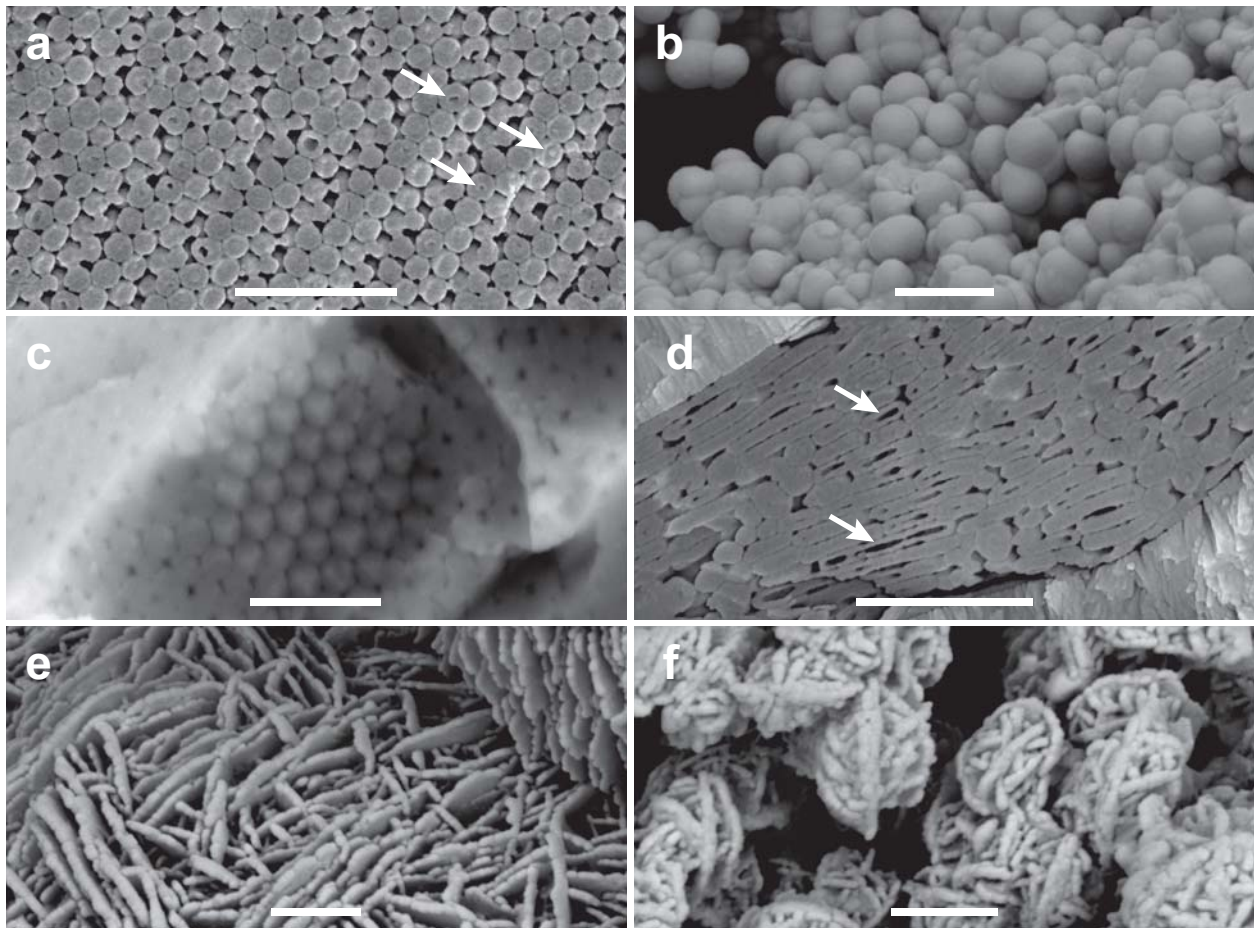
Figure 5

Figure 6
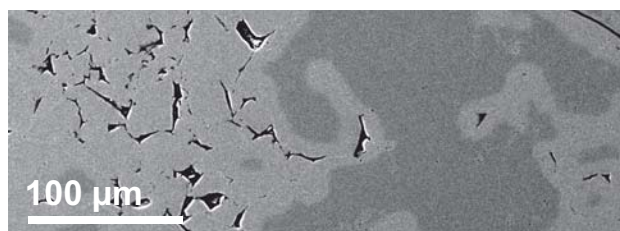
Figure 7

Figure 8

Figure 9

Figure 10