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2 Color Effects of Cu Nanoparticles in Cu-bearing Plagioclase Feldspars

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6 **Abstract**

7 The optical properties (scattering, absorption and extinction) of spheroidal Cu particles  
8 embedded in intermediate plagioclase feldspar are computed for various sizes and shapes using  
9 the Mie theory and T-matrix method. The observed color for Cu-bearing plagioclase, as a  
10 function of particle size and shape, is also calculated from the computed extinction spectra. The  
11 colors and pleochroism observed in natural and treated Cu-bearing plagioclase can be explained  
12 from the computational results. The enigmatic green colors in some precious Oregon sunstones  
13 are resulting from red light being scattered away by the Cu nanoparticles of certain sizes. The  
14 UV-VIS spectra are collected on Cu-bearing plagioclase samples for comparison with the  
15 computational results, which are shown to match the optical observations. The results from this  
16 work may be used to quantify the concentration of colloidal Cu in plagioclase, or glass with  
17 similar refractive index. Particle sizes and shapes can also be characterized using the extinction  
18 and scattering spectra, which can be collected with different optical configurations. New  
19 materials with special color effects and optical characteristics may be designed and engineered  
20 by applying the unusual properties of metal colloids.

21 **Keywords** Oregon sunstone, Cu nanoparticle, pleochroism, absorption, scattering, extinction.

## 22 **Introduction**

23 The renowned Oregon sunstone got its name from the aventurescence effect produced by the  
24 oriented copper platelets in the clear basaltic labradorite phenocrysts (Anderson 1917; Rossman  
25 2011). However, the most precious labradorites from Oregon are those with vivid red or green  
26 colors but no visible flaky inclusions (also called Oregon sunstone in the gemstone trade). It is  
27 well understood that colloidal Cu can produce red color by absorbing light below 600 nm. In  
28 fact, copper and gold nanoparticles have been used to produce red glass (often known as  
29 copper/gold ruby glass) for centuries (Freestone 1987; Brun et al. 1991; Nakai et al. 1999;  
30 Freestone et al. 2007; Ruivo et al. 2008; Drünert et al. 2018; Bandiera et al. 2019). The Cu in  
31 many gem feldspars on the market was actually artificially diffused into the crystals to produce  
32 the desired colors, creating huge controversy regarding the origin and authenticity of these semi-  
33 precious gemstones (Rossman 2011). Although the red color found in Oregon sunstones and  
34 other Cu-containing feldspars can be easily explained by the optical properties of Cu colloid  
35 (Hofmeister and Rossman 1985), the scarcer green color, on the other hand, is much more  
36 puzzling, since no glass counterpart with similar colors has been manufactured. Hofmeister and  
37 Rossman (1983) first hypothesized that anisotropic colloids could be associated with the  
38 pleochroism often observed in green Oregon sunstones, but also speculated that  $\text{Cu}^{1+}/\text{Cu}^0$   
39 intervalence charge transfer (IVCT) or  $\text{Cu}^0$  pairs may be causing the green colors (Hofmeister  
40 and Rossman 1985). Farfan and Xu (2008) reported some correlation between the Cu particle  
41 orientations and the pleochroism in Oregon Sunstone. A recent TEM study has discovered  
42 anisotropic Cu nanoparticles in a pleochroic Oregon sunstone (Wang et al. 2019), which further  
43 suggests that the green colors in Oregon sunstone may also be from colloidal Cu.

44 Most colored stones are homogeneous solutions of light-absorbing elements or point defects,  
45 whereas the feldspars containing Cu nanoparticles (Cu-sunstones) are colloid suspensions. A  
46 transparent colloid suspension is often indistinguishable from a colored solution under ambient  
47 lighting conditions, and can only be identified using the Tyndall effect with intense and  
48 directional illumination (i.e. a laser beam). The Cu particles attenuate the light entering the  
49 feldspar crystals through both absorption and scattering, creating colors in the transmitted light  
50 (Figure 1). Only the transmittance can be easily measured using a UV-VIS spectrometer, which  
51 is used to calculate the total extinction (absorption + scattering, also called attenuation). It is  
52 impossible to measure the absorbance alone using a regular spectrometer, which means all

53 previously published absorption spectra (Hofmeister and Rossman 1983, 1985; Rossman 2011)  
54 of Cu-sunstones are actually extinction (attenuation) spectra, with the assumption of zero  
55 scattering. Some recent studies (Kalenskii et al. 2015; Drünert et al. 2018), however, show that  
56 the scattering cross-section of Cu nanoparticle contributes significantly to the total extinction and  
57 cannot be ignored. The light scattered by a dilute colloid suspension in any particular direction (a  
58 tiny fraction of the total scattered light) is extremely weak and may be easily neglected.  
59 Measurement of the scattered spectrum is also very difficult, because the scattered light, often  
60 anisotropic, is attenuated before leaving the crystal (by other particles and the matrix), and can  
61 be easily overwhelmed by any background noise (reflection from the instrument parts or internal  
62 reflection from the crystal facets). On the other hand, the scattered light may also contribute to  
63 the observed color (orientation dependent) in thicker crystals with higher particle concentrations,  
64 making the color effect of the Cu-sunstones even more complicated to understand.

65 Theoretical studies on the optical properties of submicron particles have been an important topic  
66 of physics for over a century, due to its importance in chemistry, biology, material optics,  
67 atmospheric and environmental science, remote sensing, and even astronomy. The scattering and  
68 absorption of light by a single spherical particle in a homogeneous matrix was solved  
69 analytically by Gustav Mie (1908) more than a century ago, which can be applied to dispersedly  
70 distributed spherical particles of identical size. Richard Gans (1912, 1915) extended Mie's  
71 solution for spheroidal particles much smaller than the excitation wavelength. Most real world  
72 systems of submicron particles, however, involve particles of less symmetrical shapes and  
73 distributed sizes over a wide range. The computational power required to numerically model  
74 these systems increase exponentially with the complexity of such systems. Many different  
75 methods have been developed to simulate the interaction of electromagnetic radiation with  
76 submicron particles of various shapes and sizes, such as the T-Matrix method, discrete-dipole  
77 approximation, the finite-element method and the finite-difference time-domain method, each  
78 with its own advantages and disadvantages (Wriedt 2009; Parsons et al. 2010).

79 Earlier calculations of the absorption spectra for copper and other metallic nanoparticles  
80 (Doremus 1964; Doremus and Turkalo 1976; Papavassiliou 1979; Ruppin 1986; Doremus et al.  
81 1992) were mostly based on the small-size ( $R \ll \lambda$ ) approximation of the Mie theory or the Gans  
82 theory. However, as pointed out by Hutter and Fendler (2004), the extinction cross-section of  
83 larger nanoparticles ( $\varnothing > 30$  nm) is dominated by higher-order multipole absorption and

84 scattering, for which more complete solutions of Maxwell's equations are needed to model the  
85 extinction spectra. The optical properties of spherical copper nanoparticles in glass have only  
86 been accurately modeled very recently with the complete Mie theory (Kalenskii et al. 2015;  
87 Drünert et al. 2018), with the results compared to both archaeological and modern glass samples  
88 (Drünert et al. 2018). However, due to the complexity of the reduced symmetry, only a few  
89 papers have been published on the extinction spectra of spheroidal metal nanoparticles  
90 (Porstendorfer et al. 1999; Jain et al. 2006; Liu et al. 2011; Somerville et al. 2016), none of  
91 which made any connections to the color effects of the particles. Studying the color effect of  
92 copper nanoparticles would require systematic calculations of the extinction spectra over a wide  
93 range of different sizes and shapes. This type of research was previously exclusive to  
94 professionally trained physicists with a complete comprehension of the electromagnetic theories  
95 to write dedicated codes for solving specific problems. Fortunately, thanks to the broad impact of  
96 particle optics, many user-friendly algorithm and codes with more general applications have  
97 been published in recent years, making the abstract and convoluted mathematical equations  
98 accessible to more researchers interested in the subject. Therefore, the puzzling color effect of  
the Oregon sunstone and other Cu-bearing plagioclase is







192 occurs for particles of radius less than ~40 nm at wavelengths below 600 nm, peaking at ~560  
193 nm caused by the localized surface plasmon resonance (LSPR) (Petryayeva and Krull 2011). The  
194 absorption power drops dramatically for spheres larger than 40 nm in radius. The scattering  
195 power of the Cu spheres, on the other hand, is negligible for radius less than 20 nm. The  
196 scattering mainly occurs at wavelengths over 550 nm, with the scattering peak moving towards  
197 longer wavelength with larger particles. The total extinction power, therefore, is dominated by  
198 absorption for smaller particles ( $R < 35$  nm) and scattering for larger particles ( $R > 35$  nm). A  
199 second scattering peak can be observed for particles with radius larger than 70 nm. The  
200 absorption, scattering and extinction maps of spherical Cu particles in labradorite are very  
201 similar to Cu particles in glass as calculated by Drünert et al. (2018), which is expected given the  
202 similar refractive indices between feldspar and glass.

203 To illustrate how the spheroidal shape changes the optical effect of the Cu particles, the  
204 absorption, scattering and extinction power maps of three incident light orientations are plotted  
205 against wavelength and aspect ratio  $\frac{c}{a}$  for Cu spheroids with  $a = 35$  nm in Figure 4. The maps of  
206 incident light along the Z-axis ( $K_Z$ , blue arrow in Figure 2) is almost identical to the maps of  
207 incident light with the polarization plane perpendicular to the Z-axis ( $M_Z$ , red arrow in Figure 2).  
208 The peak position in the  $K_Z$  and  $M_Z$  maps does not change with the aspect ratio for prolate  
209 spheroids ( $\frac{c}{a} > 1$ ), and only slightly shifts towards longer wavelength for oblate spheroids ( $\frac{c}{a} <$   
210 1). On the other hand, the aspect ratio has a very dramatic effect on the extinction spectrum of  
211 the incident light with  $E_Z$  polarization. The extinction peak shifts quickly towards the longer  
212 wavelength with increasing  $\frac{c}{a}$  ratio in the  $E_Z$  map, getting broader and stronger at the same time.  
213 The scattering power of the spheroid decrease for  $K_Z$  and  $M_Z$  but increase for  $E_Z$  with increasing  
214  $\frac{c}{a}$  ratio, indicating that the spheroid scatters light more effectively when the polarization is  
215 aligned with its longer dimension. The Cu spheroids with other sizes behaves similarly, except  
216 the  $E_Z$  scattering peaks shifts and broadens towards the longer wavelengths with increasing  $\frac{c}{a}$   
217 ratio even faster for larger spheroids (a movie showing continuously changing maps from  $a = 0$   
218 nm to  $a = 100$  nm can be found in VIDEO-1 in Supplementary Material).

219 The size vs wavelength maps for the absorption, scattering and extinction power of Cu particles  
220 with fixed  $\frac{c}{a}$  ratios of 0.5 and 2 are plotted in Figure 5 and Figure 6. Similar to Figure 4, the  $K_Z$



221 maps are almost the same as the  $M_Z$  maps for both prolate and oblate spheroids. The only  
222 noticeable differences are that the  $M_Z$  maps show an extra peak for the oblate spheroids ( $a > 40$   
223 nm, marked with dotted ellipsoid in Figure 5), whereas the  $K_Z$  maps have an additional peak for  
224 the prolate spheroids ( $40 \text{ nm} < a < 80 \text{ nm}$ , Figure 6). These maps show more clearly how the  
225 extinction power dramatically changes with different polarization. Both the absorption and  
226 scattering power are more than 20 times stronger when the polarization of the incident light is  
227 parallel to the longer dimension of the spheroid than perpendicular to it. Similar to the spherical  
228 particles (Figure 3), absorption is the main effect for small particles and scattering quickly takes  
229 over at around  $a = 35 \text{ nm}$  with increasing particle size. The  $E_Z$  maps have similar shapes as the  
230 other orientations, except extended or contracted by a factor of  $\frac{c}{a}$ . In prolate spheroids (Figure 6),  
231 the LSPR peak in the  $E_Z$  map, which is completely separated from the absorption band at shorter  
232 wavelengths ( $\lambda < 570 \text{ nm}$ ), is much stronger than in spheres (Figure 3) or oblate spheroids  
233 (Figure 5), and strongly shifted towards longer wavelengths ( $\lambda > 620 \text{ nm}$ ). A movie showing the  
234 maps continuously transforming from Figure 5 to Figure 6 with increasing  $\frac{c}{a}$  can be found in  
235 VIDEO-2 of Supplementary Material.

236 Unlike absorption, the scattered energy by Cu particles is not immediately lost (transferred to  
237 heat) and may affect the observed color in ways other than simple extinction. Therefore, it is  
238 worth considering the spatial distribution of the scattered light. The phase functions  $F(\theta, \varphi)$   
239 (normalized scattered intensity as a function of polar angle  $\theta$  and azimuthal angle  $\varphi$  of the  
240 scattered direction) of spherical particles of radius 60 nm, 80 nm and 100 nm at  $\lambda = 600 \text{ nm}$  are  
241 plotted in Figure 7. Scattering of Cu sphere with radius of 60 nm or smaller can be  
242 approximately described by Rayleigh scattering, in which the scattered intensity is constant in  
243 the plane perpendicular to the polarization direction, and proportional to  $\cos^2\theta$  within the  
244 polarization plane. As the Cu sphere gets larger, the scattered light shifts towards the forward  
245 direction ( $\theta < 90^\circ$ ). At  $R = 100 \text{ nm}$ ,  $\sim 35\%$  of the light is scattered in the backward direction  
246 (Figure 7). Nonetheless, the energy of incident light from one direction is spread in different  
247 directions in 3D space, which means the extinction power in Figure 3-6 is a good measurement  
248 of the extinction of light in the forward direction ( $\theta = 0^\circ$ ). The phase functions of spheroidal  
249 particles are very similar to spherical particles as shown by previous studies (Asano and  
250 Yamamoto 1975; Asano 1979; Mishchenko et al. 2000, 2002a; Mishchenko and Travis 2003). It

251 is known that for given refractive indices of the particle and the matrix, the phase function,  
252 which is dimensionless, is only dependent on the ratio between the particle diameter and the  
253 wavelength (scale invariance rule) (Mishchenko et al. 2002b). This means for a fixed particle  
254 size, light with shorter wavelengths would be more preferably scattered in the forward direction  
255 relative to light with longer wavelengths. However, this effect is negligible compared to the  
256 difference in the total scattering power at different wavelengths (Figure 3), and cannot affect the  
257 observed color of Cu-sunstone.

258 Only the optical effects of the Cu particles inside plagioclase crystals have been considered so  
259 far. The feldspar crystals themselves are often light yellow colored from  $\text{Fe}^{3+}$  substitution in the  
260 framework (Hofmeister and Rossman 1983), which also contribute to the appearance of the Cu-  
261 sunstones. The extinction (attenuation) of a Cu-sunstone can be calculated by simply adding the  
262 absorbance of the feldspar to the attenuation of the Cu particles:

$$A_{\text{sun}} = A_{\text{Cu}} + A_{\text{fs}}$$

263 , in which  $A_{\text{Cu}} = 0.131(X_{\text{ext}})w_{\text{Cu}}$ . An example of the calculated extinction spectrum of a Cu-  
264 sunstone containing 10 ppmw of spherical Cu particles with 5 nm radius is shown in Figure 8.  
265 The resulting spectrum is almost identical to the experimental data reported by (Hofmeister and  
266 Rossman 1983, 1985; Susawee 2013; Susawee and Sutthirat 2014), and very similar to the  
267 absorption spectrum of the copper ruby glass studied by (Durán et al. 1984; Doremus et al. 1992;  
268 Akai et al. 1993; Nakai et al. 1999; Capatina 2005; Macalik 2005).

269 From the calculated spectrum, the observed colors (RGB values) of the Cu-sunstones can be  
270 calculated following the method by Sun et al. (2017). To best compare the color effect of Cu  
271 particles with different sizes and shapes, the computed colors are mapped against equatorial  
272 radius ( $a$ ) and aspect ratio ( $\frac{c}{a}$ ) for 3mm thick Cu-sunstones containing ~20 ppmw of Cu particles  
273 in Figure 9. These parameters are selected to produce the most saturated colors overall. Only  
274 incident light perpendicular to the rotational axis ( $M_Z$  and  $E_Z$ ) is calculated, because this is the  
275 direction with the strongest potential pleochroism, and the  $K_Z$  map would be identical to the  $M_Z$   
276 map given the similarity in the extinction power maps (Figure 4-6). The color map with  
277 unpolarized incident light is also calculated by averaging the extinction spectrum of the two  
278 polarization following the equation (Libowitzky and Rossman 1996):

$$A_{\text{unpol}} = -\log\left(\frac{10^{-A_Y} + 10^{-A_Z}}{2}\right)$$

279 A region of intense red color is resulted for particles with radius less than 35 nm in the  $M_Z$  color  
280 map. The color quickly transitions to deep green as the radius passes  $\sim 40$  nm. The color gets  
281 washed out with larger particle sizes. The  $E_Z$  color map show very similar colors, but with  
282 significantly different shapes for each region. The region of the red color extends to larger  
283 particle sizes for oblate spheroids, which contracts and disappears with increasing aspect ratio.  
284 The strongest pleochroism appears with Cu particles of  $a \sim 30$  nm and  $c \sim 40$  nm, showing deep  
285 red and green color with light polarized perpendicular and parallel to the  $Z$ -axis respectively.  
286 Oblate particles with  $a \sim 45$  nm and  $c \sim 30$  nm show similar pleochroism, but with lighter orange  
287 color for  $E_Z$  incident light. Spheroids (oblate or prolate) of smaller sizes are also slightly  
288 pleochroic, with the red color more saturated when the incident light is polarized along the  
289 longer dimensions of the spheroids. The red region in the unpolarized color map is the  
290 intersection of the red regions in both the  $M_Z$  and  $E_Z$  color maps, bounded by a strip of green  
291 region. The red color in the unpolarized color map is more homogeneous and does not change  
292 with different particle sizes or shapes. It should be noted that thicker crystals with less Cu-  
293 particle concentration may produce colors of similar saturation, but with slightly different hues.

294

## 295 **Comparison to experimental data and discussion**

296 Only metallic Cu particles are considered in this paper, as no other form of Cu-containing  
297 precipitates has been reported in feldspars, and Cu oxide particles have been shown to have  
298 completely different optical effects (Drünert et al. 2018). The optical effects of Cu particles in  
299 plagioclase feldspars are modeled with spheroids, because they are the simplest (most  
300 symmetrical) shapes possible that can create pleochroism. It is also not a bad assumption for the  
301 real Cu-sunstone, since the shapes of metallic nanoparticles are mostly controlled by minimizing  
302 its surficial or interfacial energy. Spherical shape is expected for particles in isotropic matrix  
303 such as liquid or glass, and the anisotropy of a crystal with low symmetry (such as plagioclase)  
304 may distort them into spheroids or ellipsoids. Spherical and spheroidal nanoparticles of coinage  
305 metal are often directly observed in glass or solution using transmission electron microscope  
306 (TEM) (Doremus and Turkalo 1976; Barber and Freestone 1990; Doremus et al. 1992; Link and

307 El-Sayed 1999; Kaempfe et al. 2001; Suszyńska et al. 2003, 2010; Gil et al. 2005; Macalik 2005;  
308 Bring 2006; Amendola and Meneghetti 2009; Choi et al. 2012; Pellerin et al. 2013; Boita et al.  
309 2017). Small Cu particles ( $\varnothing < 20$  nm) in plagioclase showing almost perfect spheroidal shapes  
310 have been directly observed in TEM recently (Wang et al. 2019). The larger Cu particles ( $\varnothing \sim 100$   
311 nm) in natural pleochroic Oregon sunstones reported by Xu et al. (2017) show less regular  
312 shapes, and are accompanied by nano-precipitates of protoenstatite, suggesting a more  
313 complicated exsolution process of Cu in natural plagioclase. Research on Cu precipitates in  
314 plagioclase is quite limited, mostly due to their extremely low concentration, requiring tens or  
315 even hundreds of hours on a TEM to locate and image only a handful of Cu particles. The  
316 diffusion and exsolution mechanism of Cu in feldspars is also poorly understood. Nonetheless,  
317 based on the limited observations, spheroid is a reasonable approximation for the size range  
318 calculated in this work. Particles with larger sizes, on the other hand, are expected to deviate  
319 significantly from ideal spheroidal shapes, and approach thin flakes as they grow large enough to  
320 be visible with optical microscope.

321 For comparison with the computational results, the polarized extinction spectra of the four Cu-  
322 sunstone samples are measured along the maximum (dotted line) and minimum (solid line)  
323 extinction direction (Figure 10). Images showing the sample colors under polarized transmission  
324 light corresponding to the extinction spectra are also shown with the plots. The orientation of an  
325 absorber in a triclinic crystal is not constrained by symmetry, thus independent from the  
326 orientation of the optical indicatrix (Dowty 1978; Libowitzky and Rossman 1996). The  
327 orientation effect of multiple Cu particles is even more complicated, considering the extinction  
328 power is not only dependent on the polarization, but also the incidence direction (Figure 5, 6).  
329 Measuring the average orientation of the Cu particles relative to the feldspar crystal is beyond  
330 the scope of this study, therefore the samples are only cut and polished in one orientation. The  
331 extinction spectra show a wide variety among the natural and Cu-diffused samples, resulting in  
332 different hues of green and red colors. The spectra corresponding to the red colors (minimum  
333 extinction in Figure 10a, b) are the same as previously reported ones (Hofmeister and Rossman  
334 1983, 1985; Rossman 2011). The LSPR peak at  $\sim 570$ nm is slightly broader relative to the  
335 spectrum calculated for spherical particles (Figure 8), most likely due to a dispersed distribution  
336 of particle sizes and shapes. The green-colored spectra show extinction peaks much stronger than  
337 the red ones, occurring anywhere between 590nm and 700nm. The peaks at longer wavelengths

338 are much broader than the ones at shorter wavelengths, agreeing with the calculated extinction  
339 spectra (Figure 3-6). Note that the extinction peak in the green spectrum of sample SB-001  
340 appears at ~610nm (instead of 630nm), and is much sharper than the previously reported spectra  
341 (Hofmeister and Rossman 1983, 1985; Rossman 2011). The large variations in the peak shapes  
342 and positions cannot be explained by any absorption from trace elements or intervalence charge  
343 transfers. More diverse extinction spectra are certainly expected when more natural Cu-sunstones  
344 are studied, considering the wide range of reported colors.

345 Zoomed images of sample A110 (Figure 10b) are shown in Figure 11 with different polarized  
346 illuminations. The crystal has a colorless rim of ~0.5 mm wide (typical for treated stones),  
347 followed by a 0.2mm red zone (not pleochroic), and then transfers inward to a strongly  
348 pleochroic region (green-red). It should be noted that even though the polarization of the  
349 maximum extinction (dark green color) aligns with the twin planes in the feldspar crystal, it  
350 cannot be directly used to infer the orientations of the Cu-particles. Because the light inside the  
351 sunstone is polarized following the optical indicatrix of the birefringent feldspar, which is  
352 independent from the polarization of the incident light (Libowitzky and Rossman 1996). The red  
353 zone barely scatter any light under reflective lighting, whereas the pleochroic region scatters  
354 light more expressively (Tyndall effect). The backscattered light is also strongly polarized, with  
355 much stronger scattering corresponding to the maximum extinction (green color under  
356 transmission light). This confirms the computational result, where the red color is created by  
357 strong absorption of blue and green light ( $\lambda < 600$  nm), and the green color by scattering  
358 dominated extinction (red and orange light with  $\lambda > 570$  nm being scattered away). Images of  
359 sample SB-001 under the same polarized illumination are provided in Figure S2 in  
360 Supplementary Material, showing the colors in natural Cu-sunstone are created by the same  
361 mechanism as treated stones. The red Tyndall effect in sample SB-001 is better shown in Figure  
362 S3.

363 Under unpolarized transmission light, sample A110 appears similar to Figure 11b, except with  
364 slightly lighter green color, agreeing with the color map of unpolarized light in Figure 9.  
365 However, when observed with ambient illumination and no light source directly behind the  
366 crystal, sample A110 appears mostly red, suggesting that the scattered red light also contributes  
367 to the observed color. Because light scattered by a particle at depth  $t$  from the surface is

368 attenuated by a factor of  $10^{-2(A_{Cu}+A_{fs})t}$  for the round trip from the surface, the scattered intensity  
369 by all the particles at depth  $t$  inside a crystal can be described by equation:

$$\frac{dI_{bsc}}{I_0} = 10^{-2(A_{Cu}+A_{fs})t} \frac{\rho_{fs}}{\rho_{Cu}} \langle X_{bsc} \rangle w_{Cu} dt$$

370 , in which  $\langle X_{bsc} \rangle$  is the average backscattering power of the particles (generally proportional to  
371 the total scattering power  $\langle X_{sca} \rangle$ ). Therefore, the total backscattered intensity by a crystal with  
372 total thickness of  $t$  can be described by equation:

$$I_{bsc}(t) = \frac{B_{Cu}I_0}{2(A_{Cu} + A_{fs})} (1 - 10^{-2(A_{Cu}+A_{fs})t}) = \frac{B_{Cu}}{2(A_{Cu} + A_{fs})} (I_0 - I_{tra}(2t))$$

373 , where  $B_{Cu} = 0.131\langle X_{bsc} \rangle w_{Cu}$ , which is the backscattering coefficient of the Cu particles. With  
374 increasing thickness, the backscattered intensity approaches the maximum value of  $\frac{B_{Cu}I_0}{2(A_{Cu}+A_{fs})}$   
375 twice as fast as the transmitted intensity approaches 0. This means the color of the same Cu-  
376 sunstone crystal may change from red (from the scattered light) to green (from the transmitted  
377 light) when it is cut thin enough. Note that the ratio  $\frac{B_{Cu}}{2(A_{Cu}+A_{fs})}$  approaches 0 with low Cu  
378 concentration (or small particle sizes), and converges to a constant of  $\frac{B_{Cu}}{2A_{Cu}}$  for high Cu  
379 concentration. This the reason why the best green colors are only found in larger crystals with  
380 low particle concentrations (sample SB-001 as shown in Figure S3), because the scattered light  
381 intensity is negligible and does not affect the color under most lighting conditions.

382 As shown in Figure 9, the colors created by extinction become more and more washed out  
383 (whitened) as the extinction power decreases with increasing particles sizes. This explains the  
384 scarcity of the green colors in natural Cu-sunstones, as such colors can only be created by Cu  
385 particles within a very narrow range of sizes. As the particle size increases, the enhancement of  
386 surface electric field, which is responsible for the strong scattering power for the small Cu  
387 particles, drops dramatically due to the decreasing surface curvature. This means scattering from  
388 the larger Cu particles is mostly surface reflection, which should be similar to bulk metallic Cu.  
389 For example, the scattered intensity by a Cu sphere with a radius of  $2\mu\text{m}$  is plotted against  
390 wavelength and scattering angle in Figure 12. Around 50% of the scattered energy are uniformly  
391 diffracted within the cone of  $\theta < 5^\circ$  in the forward direction. For all the scattering angles larger  
392 than  $30^\circ$ , the scattered energy shows a sharp increase around 560 nm very similar to the

393 reflectivity of bulk metallic Cu, with the longer wavelengths scattered about twice as much as the  
394 shorter wavelengths. Note that the aforementioned features are not exclusive to the spherical  
395 particles, only the ripples in the scattered intensity map is characteristic to the shape, which  
396 eventually disappear with increasing size. In fact, the extinction cross section of a large Cu  
397 particle is no longer wavelength dependent, because light is either blocked (absorption +  
398 reflection) or diffracted uniformly. Therefore, the only color that can be observed is the color of  
399 the reflected light by the Cu particles, which is almost the same as bulk metallic copper. This is  
400 actually the color of the aventurescence or “schiller” effect that the Oregon sunstones are best  
401 known for [Figure S1-4 in Xu et al. (2017)]. More total exsolved Cu may be needed for the  
402 larger particles to create an observable optical effect, due to the reduced scattering power with  
403 increasing particle sizes, even though the surface-to-volume ratio of the larger Cu particles is  
404 often compensated by flattened shapes.

405 It is also worth noting that the natural Cu-sunstone from Oregon (SB-001) shows stronger  
406 pleochroism than the Cu-diffused samples (Figure 10), suggesting stronger anisotropy and  
407 smaller deviation in the particle shapes and orientations. The Cu concentrations in the Cu-  
408 diffused samples are much higher (~10×) than the natural Oregon sunstone with similar color  
409 saturation (attenuance), indicating that a much smaller fraction of Cu has exsolved as Cu  
410 particles in the treated stones. These distinctions reflect different thermal histories between  
411 natural and treated Cu-sunstones, and may provide clues on separating untreated stones from Cu-  
412 diffused ones in a gemology lab. The labradorite phenocryst may have equilibrated with the Cu-  
413 bearing basaltic magma for over 1000 years before eruption (Ramos et al. 2005) and cooling  
414 after eruption can take months or even years (Long and Wood 1986; Petcovic and Dufek 2005),  
415 which is significantly longer than the time needed to treat the stones in a laboratory (Emmett and  
416 Douthit 2009). The protoenstatite precipitates found in natural Oregon sunstones (Xu et al.  
417 2017), as well as their complicated structural states (Jin et al. 2018, 2019), could also affect the  
418 nucleation of Cu particles. Further study on the diffusion and exsolution of Cu in plagioclase  
419 feldspars is required to fully understand the formation process of these Cu particles.

420

## 421 **Implications**

422 Metallic Cu particles alone can clearly explain all the color effects that are observed in natural  
423 and treated Cu-sunstones, without involving any other chromophores. The Cu nanoparticles  
424 creates color with a mechanism different from the other colored gemstones. Smaller particles ( $\varnothing$   
425  $< 80$  nm) mainly absorb blue and green light and allow red light to pass through, and slightly  
426 larger particles ( $80 \text{ nm} < \varnothing < 120 \text{ nm}$ ) strongly scatter red and orange light away to allow more  
427 green light through. Strong pleochroism is created when elongated particles of similar sizes are  
428 orientated in the same direction. The red Tyndall effect can be observed in green/pleochroic Cu-  
429 sunstones, but only under intense and directional lighting (i.e. fiber optic illuminator). The  
430 appearance of the Cu-sunstone is also dependent on the particle concentration and crystal size,  
431 which controls the intensity ratio between the scattered light and the transmitted light. Only a  
432 small amount ( $\sim 20$  ppmw) of exsolved Cu is needed to produce saturated colors, and the  
433 colorless rims of the Cu-sunstones contain similar amount of Cu as the colored cores, indicating  
434 that most of the Cu is dissolved in the feldspar lattice (presumably as  $\text{Cu}^+$  or  $\text{Cu}^{2+}$ ) with no  
435 detectable absorption effect in the visible light range.

436 Analyzing the concentration, as well as size and shape distribution of Cu particles in natural and  
437 treated Cu-sunstones, is essential in understanding the mechanism of the fast diffusion and  
438 exsolution process of Cu in plagioclase crystals. Absorption spectra have been regularly used in  
439 determining both the size and shape distribution of small gold and silver nanoparticles in  
440 colloidal solutions (Eustis and El-Sayed 2006; Haiss et al. 2007; Amendola and Meneghetti  
441 2009; Kolwas et al. 2009; Resano-Garcia et al. 2015; Battie et al. 2017; Ngumbi et al. 2018;  
442 Kumar et al. 2019). The size distribution of larger Cu spheres in glass has also been studied with  
443 backscattering spectra (Drünert et al. 2018). The results from this work show that these  
444 spectroscopy-based studies are not limited to small particle sizes or spherical shapes. Multiple  
445 spectra from one single sample (polarized extinction and backscattering) can also be used for  
446 more comprehensive analyses.

447 The special optical properties of metallic nano-particles have been used to create colors in  
448 glasses for centuries, and is still a hot topic in the research of optical materials. The observed  
449 colors of Cu-sunstones are not only dependent on the polarization of the incident light, but also  
450 the relative direction of the incident light to the observer. The scattering dominated extinction in  
451 Cu-sunstone provides new possibilities for designing novel materials with special color effects



452 and optical properties, if the particle sizes and shapes can be precisely controlled within a narrow  
453 range.

454

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461 **References**

- 462 Akai, T., Kadono, K., Yamanaka, H., Sakaguchi, T., Miya, M., and Wakabayashi, H. (1993)  
463 Preparation of Copper-Ruby Glasses by Sputtering and Their Optical Properties. *Journal*  
464 *of the Ceramic Society of Japan*, 101, 105–107.
- 465 Amendola, V., and Meneghetti, M. (2009) Size Evaluation of Gold Nanoparticles by UV–vis  
466 Spectroscopy. *The Journal of Physical Chemistry C*, 113, 4277–4285.
- 467 Anderson, O. (1917) Aventurine labradorite from California. *American Mineralogist*, 2, 91.
- 468 Asano, S. (1979) Light scattering properties of spheroidal particles. *Applied optics*, 18, 712–723.
- 469 Asano, S., and Yamamoto, G. (1975) Light Scattering by a Spheroidal Particle. *Applied Optics*,  
470 14, 29–49.
- 471 Babar, S., and Weaver, J.H. (2015) Optical constants of Cu, Ag, and Au revisited. *Applied*  
472 *Optics*, 54, 477–481.
- 473 Bandiera, M., Lehuédé, P., Verità, M., Alves, L., Biron, I., and Vilarigues, M. (2019)  
474 Nanotechnology in Roman Opaque Red Glass from the 2nd Century AD. *Archaeometric*  
475 *Investigation in Red Sectilia from the Decoration of the Lucius Verus Villa in Rome.*  
476 *Heritage*, 2, 2597–2611.
- 477 Barber, D.J., and Freestone, I.C. (1990) An Investigation of the Origin of the Colour of the  
478 Lycurgus Cup by Analytical Transmission Electron Microscopy. *Archaeometry*, 32, 33–  
479 45.
- 480 Battie, Y., Izquierdo-Lorenzo, I., Resano-Garcia, A., Naciri, A.E., Akil, S., Adam, P.M., and  
481 Jradi, S. (2017) Determination of gold nanoparticle shape from absorption spectroscopy  
482 and ellipsometry. *Applied Surface Science*, 421, 301–309.
- 483 Boita, J., Nicolao, L., Alves, M.C.M., and Morais, J. (2017) Controlled growth of metallic  
484 copper nanoparticles. *New Journal of Chemistry*, 41, 14478–14485.
- 485 Bring, T. (2006) Red Glass Coloration - A Colorimetric and Structural Study. Ph.D., KTH Royal  
486 Institute of Technology, Stockholm, Sweden.
- 487 Brun, N., Mazerolles, L., and Pernot, M. (1991) Microstructure of opaque red glass containing  
488 copper. *Journal of Materials Science Letters*, 10, 1418–1420.
- 489 Capatina, C. (2005) The Study of Copper Ruby Glass. *Ceramics Silikaty*, 49, 283–286.
- 490 Choi, C.S., Jo, Y.H., Kim, M.G., and Lee, H.M. (2012) Control of chemical kinetics for sub-10  
491 nm Cu nanoparticles to fabricate highly conductive ink below 150°C. *Nanotechnology*,  
492 23, 065601.

- 493 Doremus, R., Kao, S.C., and Garcia, R. (1992) Optical absorption of small copper particles and  
494 the optical properties of copper. *Applied Optics*, 31, 5773–5778.
- 495 Doremus, R.H. (1964) Optical Properties of Small Gold Particles. *The Journal of Chemical*  
496 *Physics*, 40, 2389–2396.
- 497 Doremus, R.H., and Turkalo, A.M. (1976) Electron microscopy and optical properties of small  
498 gold and silver particles in glass. *Journal of Materials Science*, 11, 903–907.
- 499 Dowty, E. (1978) Absorption optics of low-symmetry crystals — Application to titanian  
500 clinopyroxene spectra. *Physics and Chemistry of Minerals*, 3, 173–181.
- 501 Drünert, F., Blanz, M., Pollok, K., Pan, Z., Wondraczek, L., and Möncke, D. (2018) Copper-  
502 based opaque red glasses – Understanding the colouring mechanism of copper  
503 nanoparticles in archaeological glass samples. *Optical Materials*, 76, 375–381.
- 504 Durán, A., Fernández Navarro, J.M., García Solé, J., and Agulló-López, F. (1984) Study of the  
505 colouring process in copper ruby glasses by optical and EPR spectroscopy. *Journal of*  
506 *Materials Science*, 19, 1468–1475.
- 507 Emmett, J.L., and Douthit, T.R. (2009) Copper Diffusion in Plagioclase p. 15. *GIA News from*  
508 *Research, GIA*.
- 509 Eustis, S., and El-Sayed, M.A. (2006) Determination of the aspect ratio statistical distribution of  
510 gold nanorods in solution from a theoretical fit of the observed inhomogeneously  
511 broadened longitudinal plasmon resonance absorption spectrum. *Journal of Applied*  
512 *Physics*, 100, 044324.
- 513 Farfan, G., and Xu, H. (2008) Pleochroism in calcic labradorite from Oregon: Effects from size  
514 and orientation of nano- and micro-precipitates of copper and pyroxene. In *Geochimica et*  
515 *Cosmochimica Acta* Vol. 72, p. A256. Presented at the Goldschmidt, Vancouver, BC,  
516 Canada.
- 517 Fitio, V., Yaremchuk, I., Vernyhor, O., and Bobitski, Y. (2020) Analytical expressions for  
518 spectral dependences of silver, gold, copper and aluminum dielectric permittivity. *Optica*  
519 *Applicata*, 50, 171–184.
- 520 Freestone, I. (1987) Composition and microstructure of early opaque red glass. *Early Vitreous*  
521 *Materials*, 173–191.
- 522 Freestone, I., Meeks, N., Sax, M., and Higgitt, C. (2007) The Lycurgus Cup — A Roman  
523 nanotechnology. *Gold Bulletin*, 40, 270–277.
- 524 Gans, R. (1912) Über die Form ultramikroskopischer Goldteilchen. *Annalen der Physik*, 342,  
525 881–900.
- 526 ——— (1915) Über die Form ultramikroskopischer Silberteilchen. *Annalen der Physik*, 352,  
527 270–284.

- 528 Gil, C., Villegas, M.A., and Fernandez Navarro, J.M. (2005) Preparation and study of  
529 superficially coloured lead glass. *Journal of Materials Science*, 40, 6201–6206.
- 530 Haiss, W., Thanh, N.T.K., Aveyard, J., and Fernig, D.G. (2007) Determination of Size and  
531 Concentration of Gold Nanoparticles from UV–Vis Spectra. *Analytical Chemistry*, 79,  
532 4215–4221.
- 533 Hofmeister, A.M., and Rossman, G.R. (1983) COLOR in FELDSPARS. In P.H. Ribbe, Ed.,  
534 Feldspar Mineralogy pp. 271–280. Mineralogical Society of American, Washington, D.C.
- 535 ——— (1984) Determination of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  concentrations in feldspar by optical-absorption  
536 and electron-paramagnetic-res spectroscopy. *Physics and Chemistry of Minerals*, 11,  
537 213–224.
- 538 ——— (1985) Exsolution of metallic copper from Lake County labradorite. *Geology*, 13, 644–  
539 647.
- 540 Hutter, E., and Fendler, J.H. (2004) Exploitation of Localized Surface Plasmon Resonance.  
541 *Advanced Materials*, 16, 1685–1706.
- 542 Jain, P.K., Lee, K.S., El-sayed, I.H., and El-sayed, M.A. (2006) Calculated absorption and  
543 scattering properties of gold nanoparticles of different size, shape, and composition:  
544 applications in biological imaging and biomedicine. *J. Phys. Chem. B*, 7238–7248.
- 545 Jin, S., Wang, X., and Xu, H. (2018) Revisiting the  $I\bar{1}$  structures of high-temperature Ca-rich  
546 plagioclase feldspar — a single-crystal neutron and X-ray diffraction study. *Acta*  
547 *Crystallographica Section B*, 74, 152–164.
- 548 Jin, S., Xu, H., Wang, X., Zhang, D., Jacobs, R., and Morgan, D. (2019) The incommensurately  
549 modulated structures of volcanic plagioclase: displacement, ordering and phase  
550 transition. *Acta Crystallographica Section B*, 75, 643–656.
- 551 Kaempfe, M., Seifert, G., Berg, K.-J., Hofmeister, H., and Graener, H. (2001) Polarization  
552 dependence of the permanent deformation of silver nanoparticles in glass by ultrashort  
553 laser pulses. *The European Physical Journal D*, 16, 237–240.
- 554 Kalenskii, A.V., Zvekov, A.A., Nikitin, A.P., and Anan'eva, M.V. (2015) Optical Properties of  
555 Copper Nanoparticles. *Russian Physics Journal*, 58, 1098–1104.
- 556 Kolwas, K., Derkachova, A., and Shopa, M. (2009) Size characteristics of surface plasmons and  
557 their manifestation in scattering properties of metal particles. *Journal of Quantitative*  
558 *Spectroscopy and Radiative Transfer*, 110, 1490–1501.
- 559 Kumar, R., Binetti, L., Nguyen, T.H., Alwis, L.S.M., Agrawal, A., Sun, T., and Grattan, K.T.V.  
560 (2019) Determination of the Aspect-ratio Distribution of Gold Nanorods in a Colloidal  
561 Solution using UV-visible absorption spectroscopy. *Scientific Reports*, 9, 17469.

- 562 Laven, P. (2003) Simulation of rainbows, coronas, and glories by use of Mie theory. Applied  
563 Optics, 42, 436–444.
- 564 ——— (2004) Simulation of rainbows, coronas and glories using Mie theory and the Debye  
565 series. Journal of Quantitative Spectroscopy and Radiative Transfer, 89, 257–269.
- 566 Libowitzky, E., and Rossman, G.R. (1996) Principles of quantitative absorbance measurements  
567 in anisotropic crystals. Physics and Chemistry of Minerals, 23, 319–327.
- 568 Link, S., and El-Sayed, M.A. (1999) Spectral Properties and Relaxation Dynamics of Surface  
569 Plasmon Electronic Oscillations in Gold and Silver Nanodots and Nanorods. The Journal  
570 of Physical Chemistry B, 103, 8410–8426.
- 571 Liu, P., Liu, Juan, Liu, Jing, Zhao, X., Xie, J., and Wang, Y. (2011) Scattering properties of an  
572 individual metallic nano-spheroid by the incident polarized light wave. Optics  
573 Communications, 284, 1076–1081.
- 574 Long, P.E., and Wood, B.J. (1986) Structures, textures, and cooling histories of Columbia River  
575 basalt flows. GSA Bulletin, 97, 1144–1155.
- 576 Macalik, B. (2005) Optical properties of copper nanoparticles in soda-lime silicate glasses.  
577 physica status solidi (c), 2, 608–611.
- 578 McClure, S.F. (2009) Observations on Identification of Treated Feldspar p. 12. GIA News from  
579 Research, GIA, Carlsbad, CA, USA.
- 580 McPeak, K.M., Jayanti, S.V., Kress, S.J.P., Meyer, S., Iotti, S., Rossinelli, A., and Norris, D.J.  
581 (2015) Plasmonic Films Can Easily Be Better: Rules and Recipes. ACS Photonics, 2,  
582 326–333.
- 583 Mie, G. (1908) Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. Annalen  
584 der Physik, 330, 377–445.
- 585 Mishchenko, M.I., and Travis, L.D. (2003) Electromagnetic scattering by nonspherical particles.  
586 In Exploring the Atmosphere by Remote Sensing Techniques pp. 77–127. Springer,  
587 Berlin, Heidelberg.
- 588 Mishchenko, M.I., Hovenier, J.W., and Travis, L.D., Eds. (2000) Light Scattering by  
589 Nonspherical Particles: Theory, Measurements, and Applications, 721 p. IOP Publishing.
- 590 Mishchenko, M.I., Travis, L.D., and Lacis, A.A. (2002a) Scattering and absorption properties of  
591 nonspherical particles. In Scattering, Absorption, and Emission of Light by Small  
592 Particles pp. 279–359. Cambridge University Press/NASA, Cambridge, United Kingdom.
- 593 ——— (2002b) T-matrix method and Lorenz-Mie theory. In Scattering, Absorption, and  
594 Emission of Light by Small Particles pp. 115–190. Cambridge University Press/NASA,  
595 Cambridge, United Kingdom.

- 596 Nakai, I., Numako, C., Hosono, H., and Yamasaki, K. (1999) Origin of the Red Color of  
597 Satsuma Copper-Ruby Glass as Determined by EXAFS and Optical Absorption  
598 Spectroscopy. *Journal of the American Ceramic Society*, 82, 689–695.
- 599 Ngumbi, P.K., Mugo, S.W., and Ngaruiya, J.M. (2018) Determination of Gold Nanoparticles  
600 Sizes via Surface Plasmon Resonance. *IOSR Journal of Applied Chemistry*, 11, 25–29.
- 601 Papavassiliou, G.C. (1979) Optical properties of small inorganic and organic metal particles.  
602 *Progress in Solid State Chemistry*, 12, 185–271.
- 603 Parsons, J., Burrows, C.P., Sambles, J.R., and Barnes, W.L. (2010) A comparison of techniques  
604 used to simulate the scattering of electromagnetic radiation by metallic nanostructures.  
605 *Journal of Modern Optics*, 57, 356–365.
- 606 Pellerin, N., Blondeau, J.-P., Noui, S., Allix, M., Ory, S., Veron, O., De Sousa Meneses, D., and  
607 Massiot, D. (2013) Control of selective silicate glass coloration by gold metallic  
608 nanoparticles: structural investigation, growth mechanisms, and plasmon resonance  
609 modelization. *Gold Bulletin*, 46, 243–255.
- 610 Petcovic, H.L., and Dufek, J.D. (2005) Modeling magma flow and cooling in dikes: Implications  
611 for emplacement of Columbia River flood basalts. *Journal of Geophysical Research:*  
612 *Solid Earth*, 110, B10201.
- 613 Petryayeva, E., and Krull, U.J. (2011) Localized surface plasmon resonance: Nanostructures,  
614 bioassays and biosensing — A review. *Analytica Chimica Acta*, 706, 8–24.
- 615 Porstendorfer, J., Berg, K.-J., and Berg, G. (1999) Calculation of extinction and scattering  
616 spectra of large spheroidal gold particles embedded in a glass matrix. *Journal of*  
617 *Quantitative Spectroscopy and Radiative Transfer*, 63, 479–486.
- 618 Ramos, F.C., Wolff, J.A., and Tollstrup, D.L. (2005) Sr isotope disequilibrium in Columbia  
619 River flood basalts: Evidence for rapid shallow-level open-system processes. *Geology*,  
620 33, 457–460.
- 621 Resano-Garcia, A., Battie, Y., Naciri, A.E., Akil, S., and Chaoui, N. (2015) Experimental and  
622 theoretical determination of the plasmonic responses and shape distribution of colloidal  
623 metallic nanoparticles. *The Journal of Chemical Physics*, 142, 134108.
- 624 Rossman, G.R. (2011) The Chinese Red Feldspar Controversy: Chronology of Research Through  
625 July 2009. *Gems & Gemology*, 47, 16-30.
- 626 Ruivo, A., Gomes, C., Lima, A., Botelho, M.L., Melo, R., Belchior, A., and Pires de Matos, A.  
627 (2008) Gold nanoparticles in ancient and contemporary ruby glass. *Journal of Cultural*  
628 *Heritage*, 9, e134–e137.
- 629 Ruppin, R. (1986) Optical absorption of copper colloids in photochromic glasses. *Journal of*  
630 *Applied Physics*, 59, 1355–1359.

- 631 Santillán, J.M.J., Videla, F.A., Scaffardi, L.B., and Schinca, D.C. (2013) Plasmon Spectroscopy  
632 for Subnanometric Copper Particles: Dielectric Function and Core–Shell Sizing.  
633 *Plasmonics*, 8, 341–348.
- 634 Scaffardi, L.B., and Tocho, J.O. (2006) Size dependence of refractive index of gold  
635 nanoparticles. *Nanotechnology*, 17, 1309–1315.
- 636 Somerville, W.R.C., Auguié, B., and Le Ru, E.C. (2016) SMARTIES: User-friendly codes for  
637 fast and accurate calculations of light scattering by spheroids. *Journal of Quantitative*  
638 *Spectroscopy and Radiative Transfer*, 174, 39–55.
- 639 Sun, Z., Palke, A.C., Muyal, J., and McMurtry, R. (2017) How to facet gem-quality chrysoberyl:  
640 Clues from the relationship between color and pleochroism, with spectroscopic analysis  
641 and colorimetric parameters. *American Mineralogist*, 102, 1747–1758.
- 642 Susawee, N. (2013) Cause of Red Coloring in Gem Plagioclase Feldspar. Masters Thesis,  
643 Chulalongkorn University, Bangkok, Thailand.
- 644 Susawee, N., and Sutthirat, C. (2014) Identification of Natural and Treated Red Feldspar.  
645 *Bulletin of Earth Sciences of Thailand*, 6, 51–66.
- 646 Suszyńska, M., Krajczyk, L., and Mazurkiewicz, Z. (2003) TEM studies of silver nanoparticles  
647 in phase-separated soda lime silicate glasses. *Materials Chemistry and Physics*, 81, 404–  
648 406.
- 649 Suszyńska, M., Morawska-Kowal, T., and Krajczyk, L. (2010) Optical properties of small silver  
650 particles embedded in soda-lime silica glasses. *Optica Applicata*, 40, 397–401.
- 651 Wang, C., Shen, A.H., Palke, A.C., and Heaney, P.J. (2019) Color origin of the Oregon sunstone  
652 pp. 71–74. Presented at the 36th International Gemmological Conference IGC, Nantes  
653 France.
- 654 Wriedt, T. (2009) Light scattering theories and computer codes. *Journal of Quantitative*  
655 *Spectroscopy and Radiative Transfer*, 110, 833–843.
- 656 Xu, H., Hill, T.R., Konishi, H., and Farfan, G. (2017) Protoenstatite: A new mineral in Oregon  
657 sunstones with “watermelon” colors. *American Mineralogist*, 102, 2146–2149.

658 Figure 1 Schematic diagram illustrating light interaction with nanoparticles in a colloid  
659 suspension. The wavy lines represent the energy absorbed by the particles and dissipated  
660 as heat. It is impossible to measure absorption independently, only the total extinction  
661 (absorption + scattering) can be calculated from transmittance. All published absorption  
662 spectra are actually extinction spectra by assuming zero scattering. The scattered light in  
663 any particular direction may be imperceptible, but the total scattering (all directions  
664 combined) can have a significant extinction effect.

665 Figure 2 Coordinates used for calculation defined relative to the spheroid, along with the  
666 orientations of the three linearly polarized incident light. Because of the rotational  
667 symmetry of the spheroid along the Z-axis, the effect of the incident light would not  
668 change with any rotation around the Z-axis. Therefore, the three orientations of incident  
669 light can be unambiguously described as  $K_z$ ,  $M_z$  and  $E_z$ .

670 Figure 3 The absorption, scattering and extinction power of spherical particles plotted against  
671 wavelength and radius. The color map is plotted in log scale for easy comparison. The  
672 same color map in linear color scale can be found in Figure S1 in Supplementary  
673 Material for better contrast.

674 Figure 4 The absorption, scattering and extinction power plotted against wavelength (400 nm -  
675 1000 nm) and aspect ratio ( $0.5 < \frac{c}{a} < 2$ ) of spheroid Cu particles with equatorial radius  $a$   
676 = 35 nm for all three incident light orientations. The same log color scale as Figure 3 is  
677 used.

678 Figure 5 The absorption, scattering and extinction power, of three incident light orientations,  
679 plotted against wavelength (400 nm – 1000 nm) and equatorial radius (0 – 100 nm) for  
680 oblate Cu spheroid with  $\frac{c}{a} = 0.5$ . The same log color scale as Figure 3 and 4 is used.

681 Figure 6 The absorption, scattering and extinction power, of three incident light orientations,  
682 plotted against wavelength (400 nm – 1000 nm) and equatorial radius (0 – 100 nm) for  
683 prolate Cu spheroid with  $\frac{c}{a} = 2$ . The same log color scale as Figure 3, 4 and 5 is used.

684 Figure 7 The phase functions  $F(\theta, \varphi)$  (normalized intensity of scattered light at a given  
685 direction) of spherical particles with radius of 60, 80 and 100 nm for  $\lambda = 600$  nm, plotted  
686 as enclosed surfaces in spherical coordinates. The direction and polarization plane of the  
687 incident light are marked with red arrows and purple planes. The vertical red plane  
688 separates the forward scattered light from the backscattered light. Note that the surface is  
689 plotted as  $3\sqrt[3]{F(\theta, \varphi)}$ , so that the scattered energy is represented by the volume of the  
690 cone in a given direction (apex at the origin), instead of the distance from the surface to



691 the origin. The total enclosed volume of the surface is therefore always 1. For  $R \ll \lambda$ , the  
692 light is scattered evenly along all directions (perpendicular to polarization). The scattered  
693 intensity shifts towards the forward direction with increasing size of the particle.

694 Figure 8 The calculated extinction (attenuation) spectrum of a Cu-colored labradorite crystal  
695 containing 10ppm of spherical Cu particles of radius of 5 nm, which is the sum of the  
696 absorption spectrum of sample DD-012 (Cu-free labradorite) and the calculated  
697 extinction spectrum of the Cu particle. The orientation dependence of the  $\text{Fe}^{3+}$  absorption  
698 band in feldspar is insignificant (Hofmeister and Rossman 1983, 1984), therefore  
699 neglected in this study.

700 Figure 9 The calculated color of Cu-sunstones (3mm thick with 20 ppmw of Cu particles) plotted  
701 against the aspect ratio ( $0.5 < \frac{c}{a} < 2$ ) and the equatorial radius ( $0 \text{ nm} < a < 100 \text{ nm}$ ) of  
702 the Cu spheroids, with linearly polarized incident light ( $M_z$  and  $E_z$ ). Color with  
703 unpolarized light is also calculated by averaging the attenuation of the two perpendicular  
704 polarizations.

705 Figure 10 Measured polarized extinction spectra of the four Cu-sunstone samples, (a) SB-001,  
706 (b) A110, (c) A112 and (d) A090, along with the images of the samples under  
707 transmission light with the same polarization. The spectra for maximum and minimum  
708 extinction are plotted in dotted and solid lines respectively. The spectra are measured in  
709 the areas with green color (at maximum extinction).

710 Figure 11 Sample A110 (Figure 10b) under plane polarized transmission light (a), (b) and  
711 reflective light (c), (d). The polarization directions are marked with cyan arrows. The  
712 pleochroic area of the crystal [green area in (b)] scatters back strongly polarized red light  
713 matching the extinction under transmission light (stronger backscattering with  
714 polarization of maximum extinction).

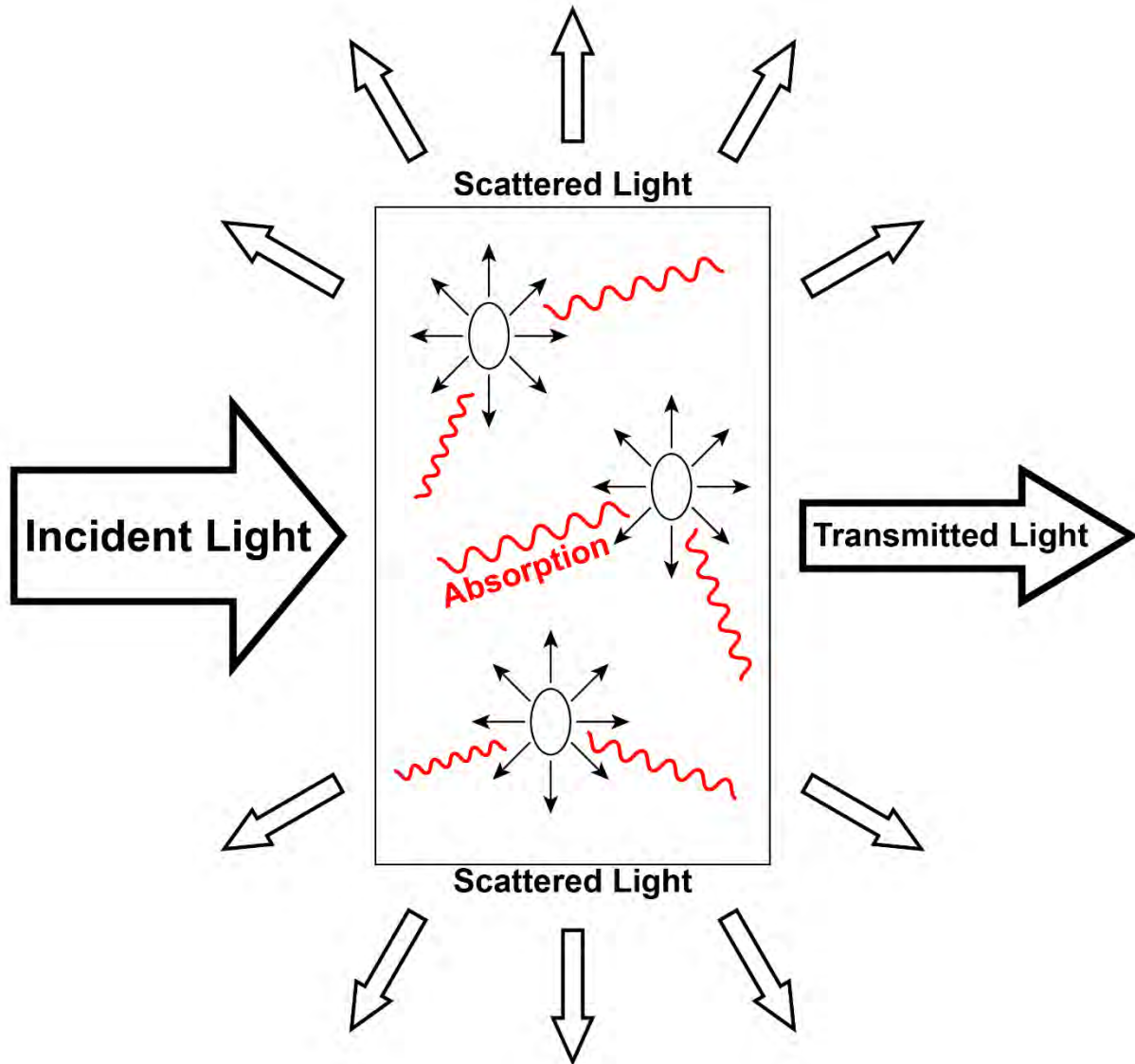
715 Figure 12 The scattered intensity (energy density) by a Cu sphere with a radius of  $2\mu\text{m}$  plotted  
716 against wavelength and scattering angle. Around 50% of the total scattered energy are  
717 diffracted within  $5^\circ$  of the forward direction ( $\theta < 5^\circ$ ), and the rest of the scattered energy  
718 is almost evenly distributed in all the other directions. For scattering angle larger than  
719  $30^\circ$ , the scattered energy shows a sharp increase around 560 nm, with the longer  
720 wavelengths scattered about twice as intense as the shorter wavelengths.

741 Table 1 Chemical formula of the major feldspar elements normalized to 4 (Al + Si) from the LA-  
 742 ICP-MS results.

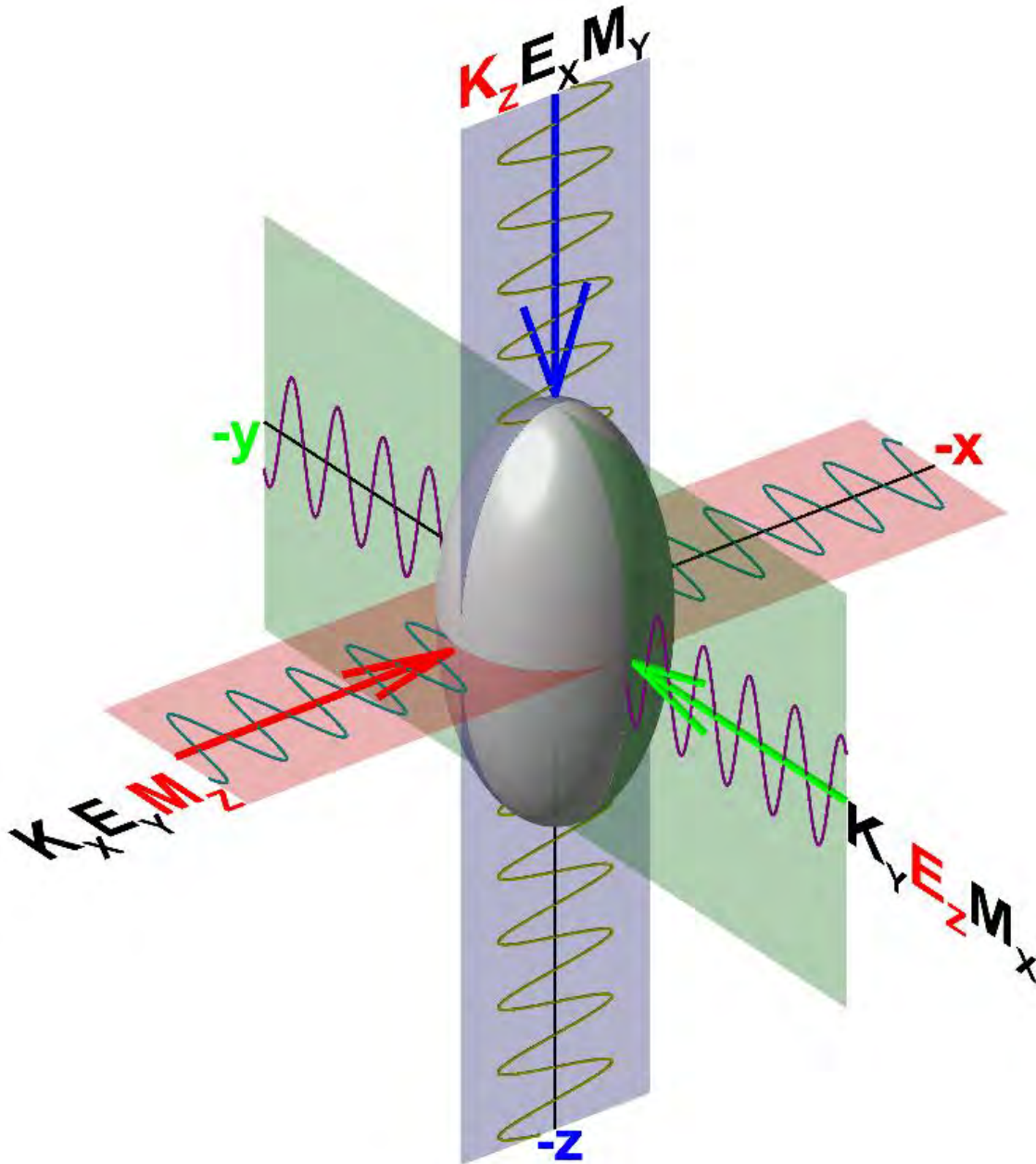
	<b>Ca</b>	<b>Na</b>	<b>K</b>	<b>Al</b>	<b>Si</b>	<b>Composition</b>
DD-012	0.648	0.334	0.007	1.643	2.357	An <sub>65.5</sub> Ab <sub>33.8</sub> Or <sub>0.7</sub>
	0.641	0.331	0.007	1.643	2.357	An <sub>65.5</sub> Ab <sub>33.8</sub> Or <sub>0.7</sub>
SB-001	0.688	0.312	0.006	1.660	2.340	An <sub>68.3</sub> Ab <sub>31.0</sub> Or <sub>0.6</sub>
	0.671	0.312	0.006	1.648	2.352	An <sub>67.9</sub> Ab <sub>31.5</sub> Or <sub>0.6</sub>
A110	0.467	0.478	0.028	1.474	2.526	An <sub>48.0</sub> Ab <sub>49.2</sub> Or <sub>2.8</sub>
	0.472	0.480	0.027	1.454	2.546	An <sub>48.2</sub> Ab <sub>49.0</sub> Or <sub>2.8</sub>
A112	0.449	0.501	0.030	1.419	2.581	An <sub>45.8</sub> Ab <sub>51.1</sub> Or <sub>3.1</sub>
	0.444	0.496	0.030	1.412	2.588	An <sub>45.8</sub> Ab <sub>51.1</sub> Or <sub>3.1</sub>
A090	0.460	0.480	0.027	1.474	2.526	An <sub>47.6</sub> Ab <sub>49.6</sub> Or <sub>2.8</sub>
	0.471	0.475	0.027	1.460	2.540	An <sub>48.4</sub> Ab <sub>48.8</sub> Or <sub>2.8</sub>

743  
 744 Table 2 Concentrations of selected trace elements from the LA-ICP-MS in ppmw. The limit of  
 745 detection for each element is listed below the element.

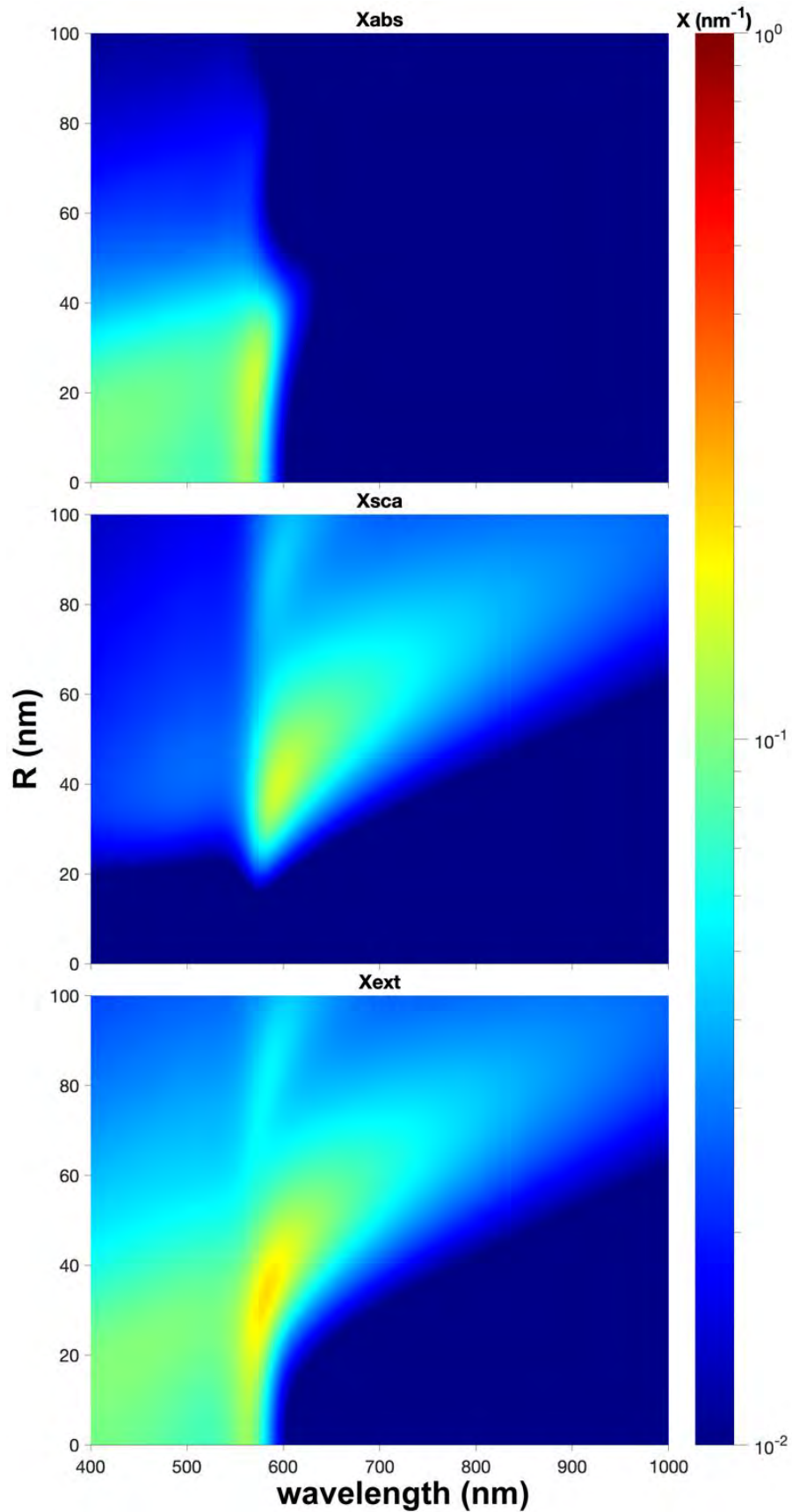
	<b>Li</b>	<b>Mg</b>	<b>P</b>	<b>Ti</b>	<b>Mn</b>	<b>Fe</b>	<b>Cu</b>	<b>Ga</b>	<b>Sr</b>	<b>Ba</b>	<b>Pb</b>
	<i>0.113</i>	<i>0.032</i>	<i>1.304</i>	<i>0.146</i>	<i>0.021</i>	<i>0.704</i>	<i>0.015</i>	<i>0.003</i>	<i>0.001</i>	<i>0.002</i>	<i>0.002</i>
DD-012	2.04	840	23.9	230	41.8	3096	0.46	16.9	642	65.5	0.17
	2.02	835	27.3	232	41.8	3091	0.30	17.0	628	65.4	0.17
SB-001	19.1	891	28.3	259	49.2	3537	47	17.2	590	62.4	0.15
	18.9	906	29.3	249	46.9	3407	49	16.7	580	63.2	0.15
A110	29.9	465	50.7	406	29.8	2622	677	19.9	1115	140	0.41
	29.7	468	51.6	402	30.4	2619	667	19.8	1101	138	0.40
A112	10.8	452	51.7	408	30.3	2658	501	19.9	1064	142	0.44
	11.4	423	55.8	412	30.1	2635	511	20.0	1062	148	0.45
A090	15.7	445	53.4	392	29.0	2539	470	19.8	1094	134	0.47
	15.0	456	52.0	403	30.0	2635	468	20.1	1120	142	0.41



746  
747 Figure 1

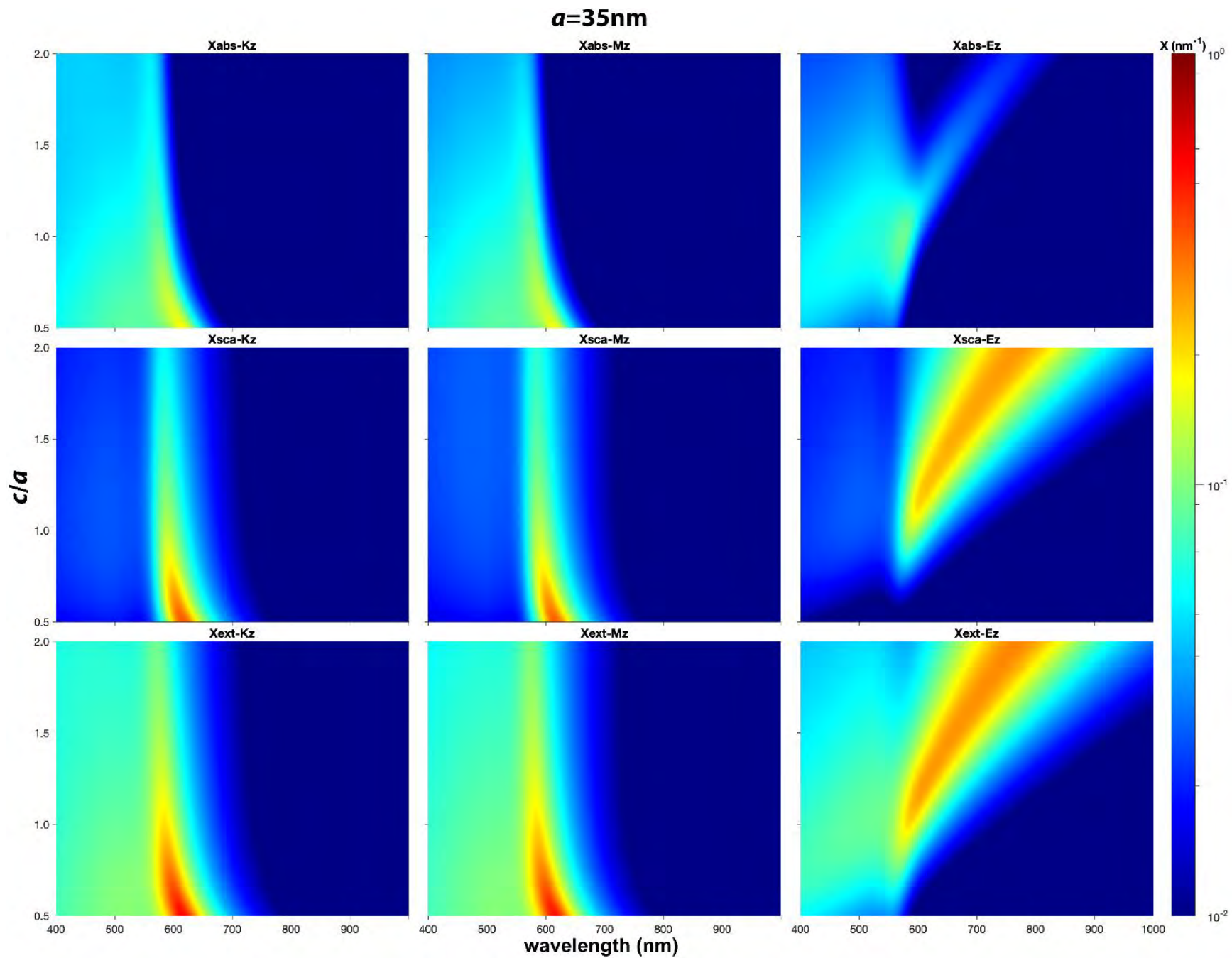


748  
749 Figure 2



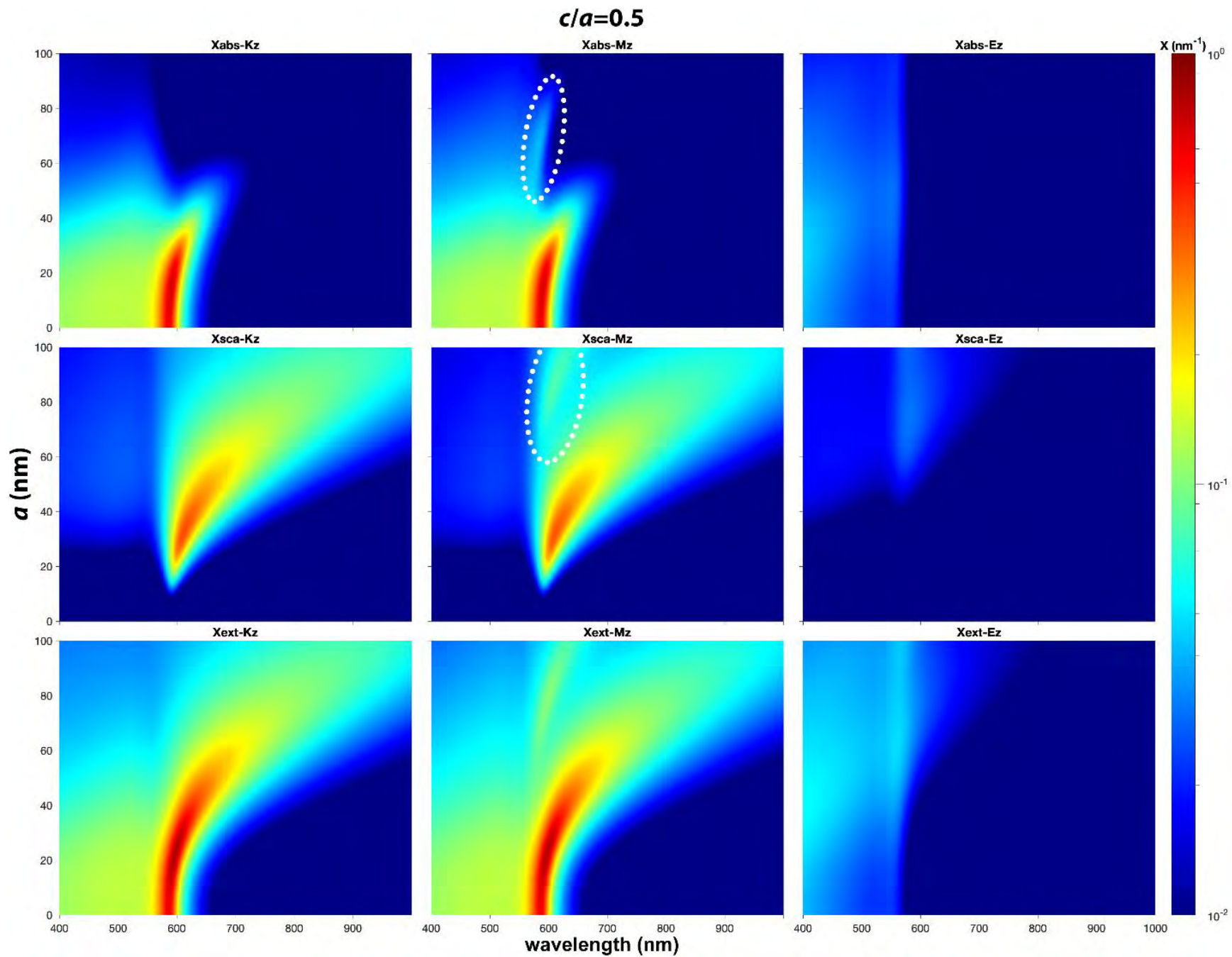
750

Figure 3

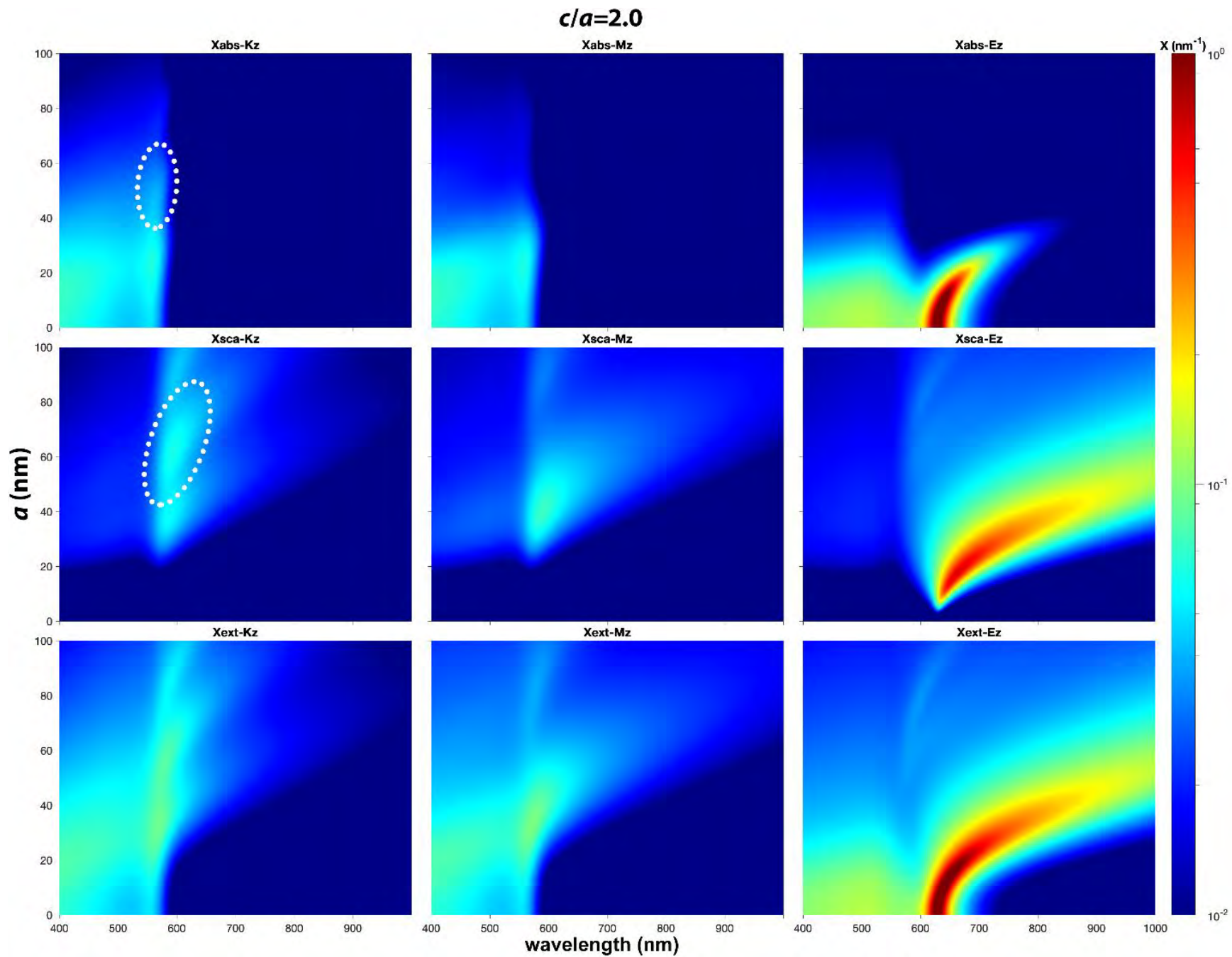


751  
752 Figure 4



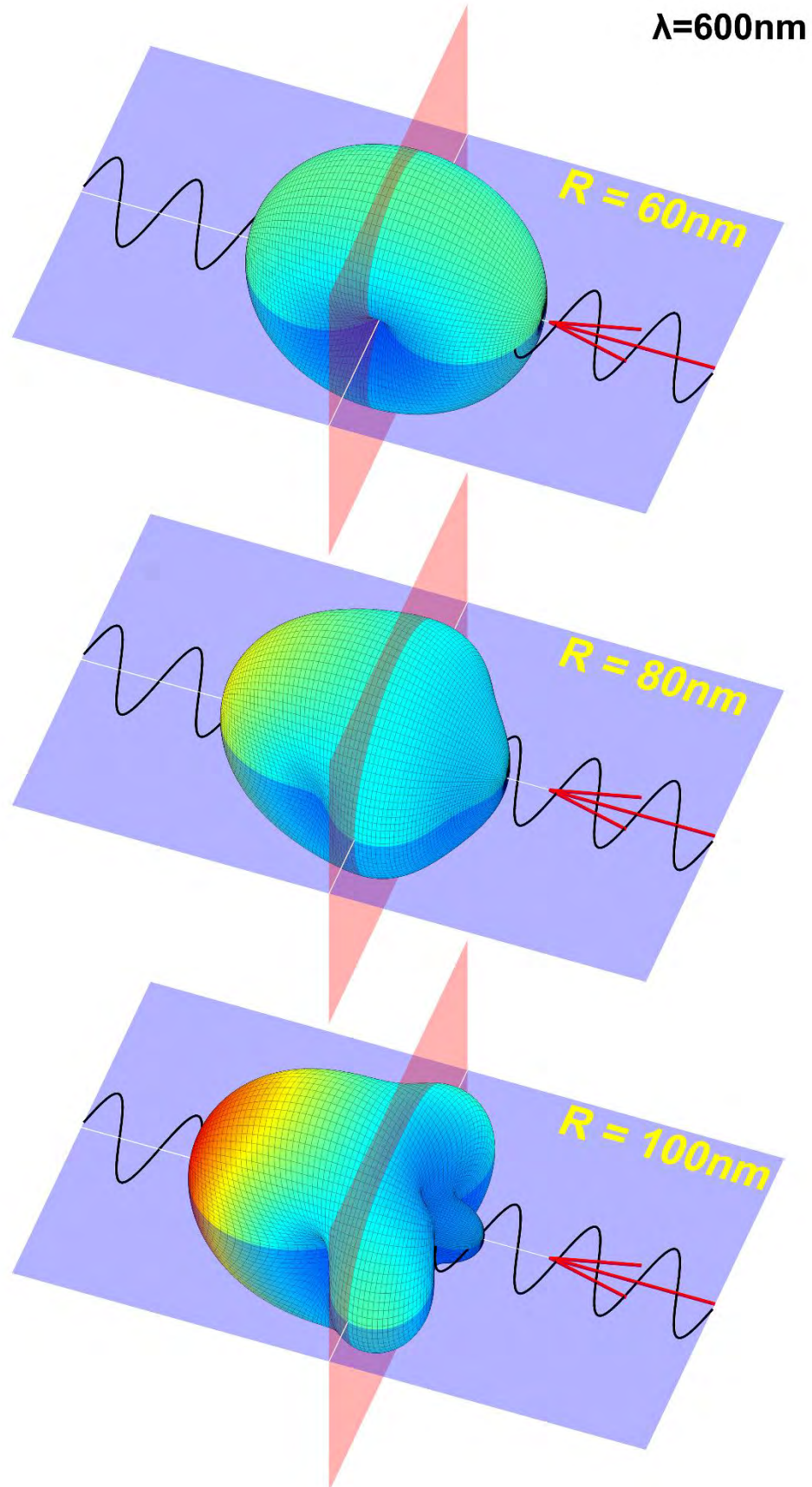


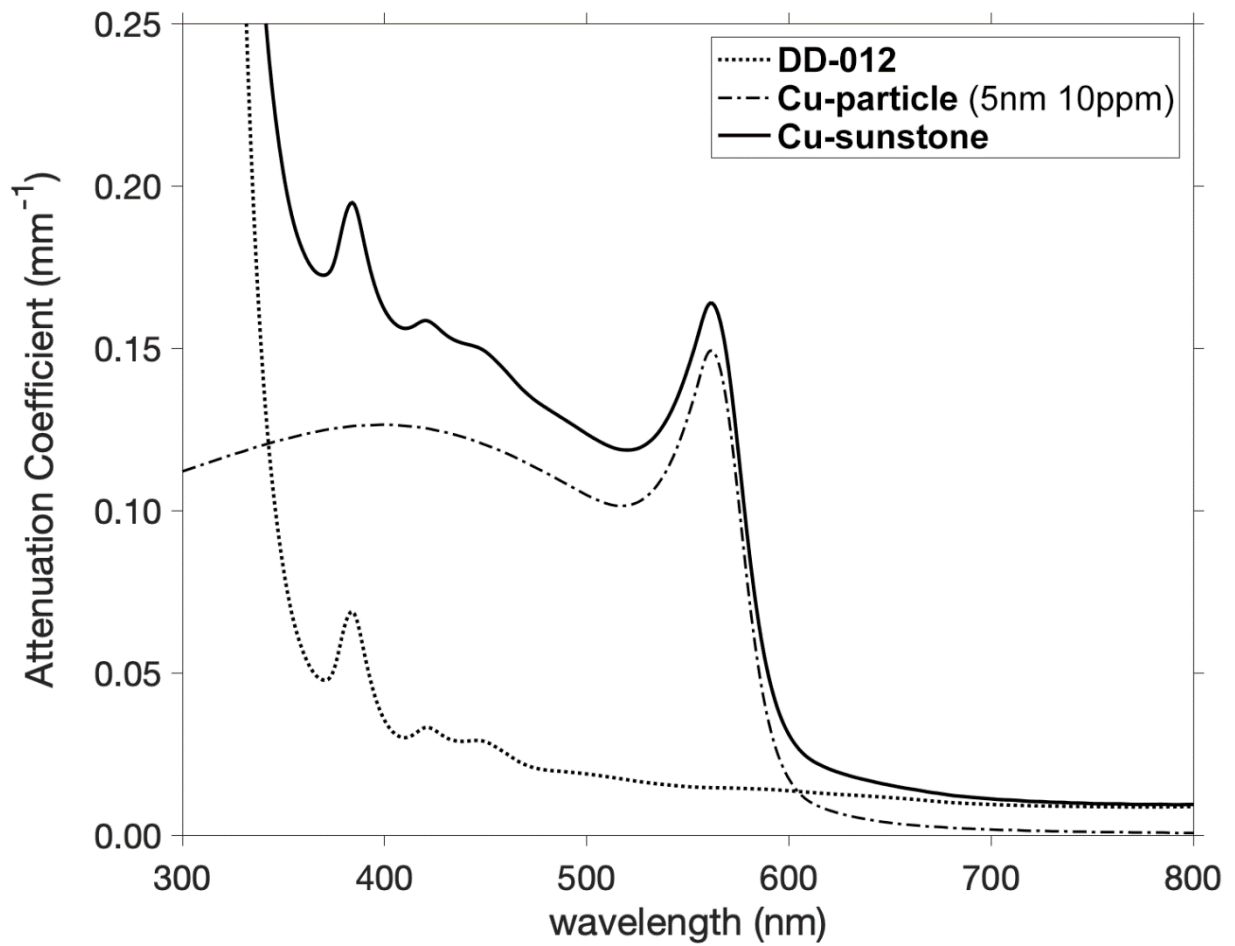
753  
754 Figure 5



755  
756 Figure 6

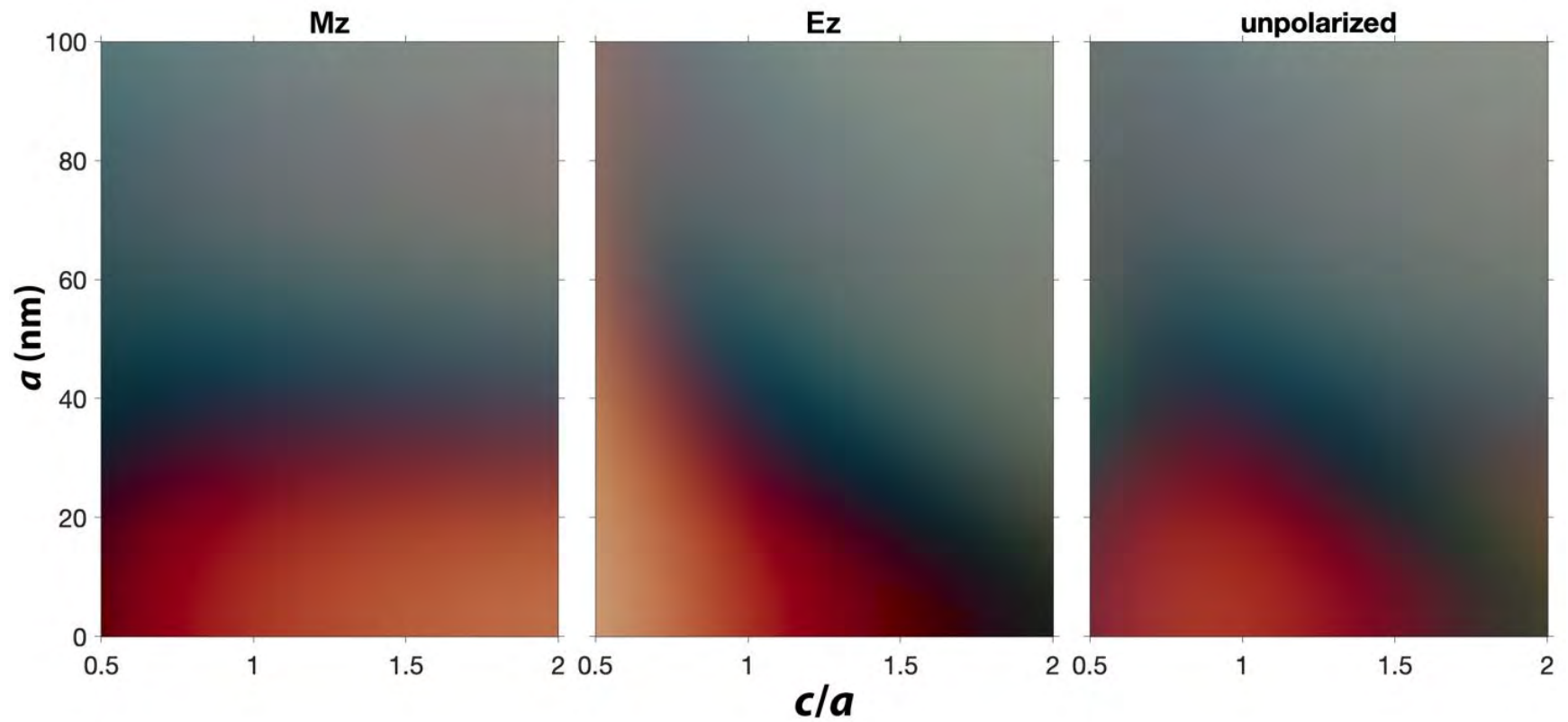






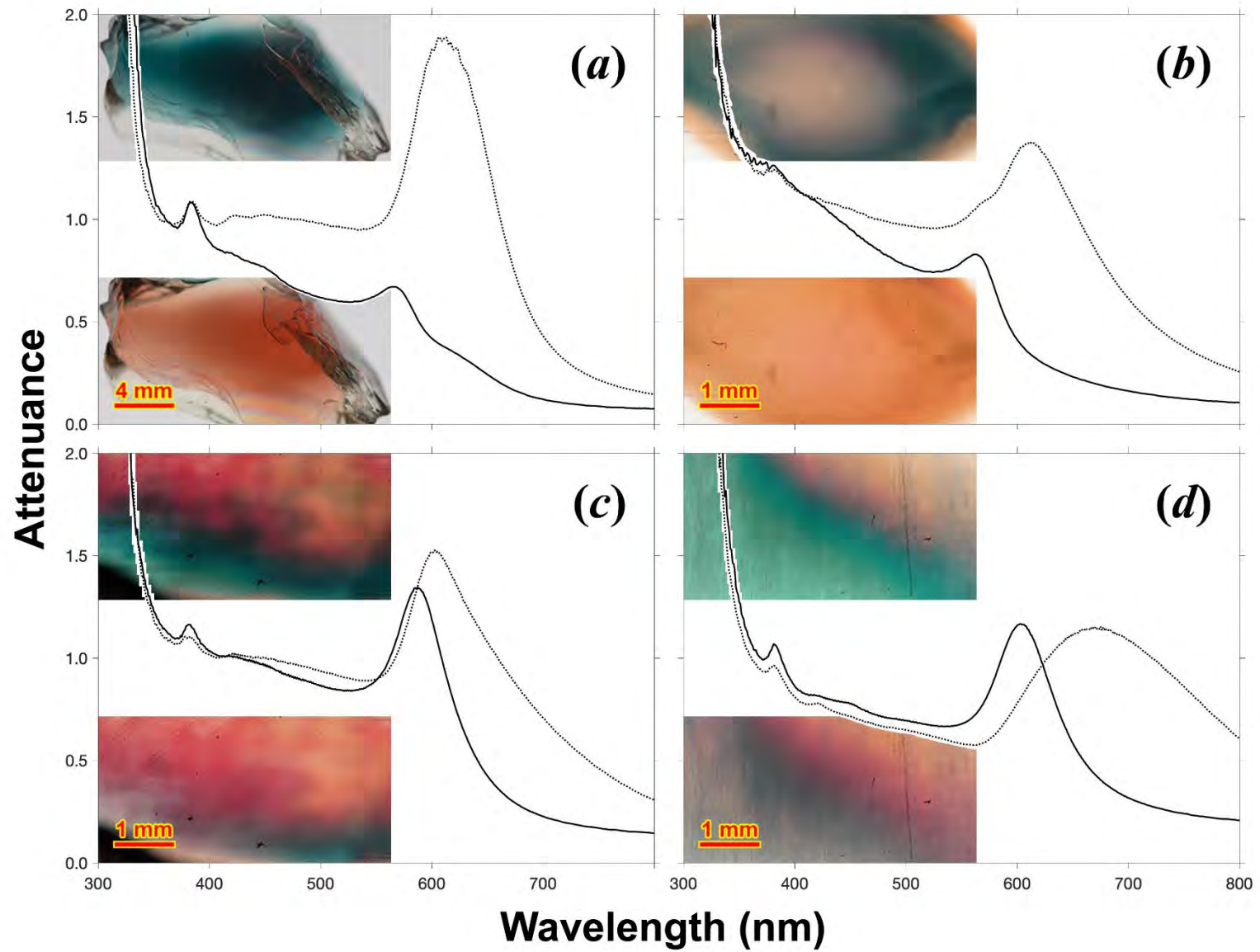
758  
759

Figure 8



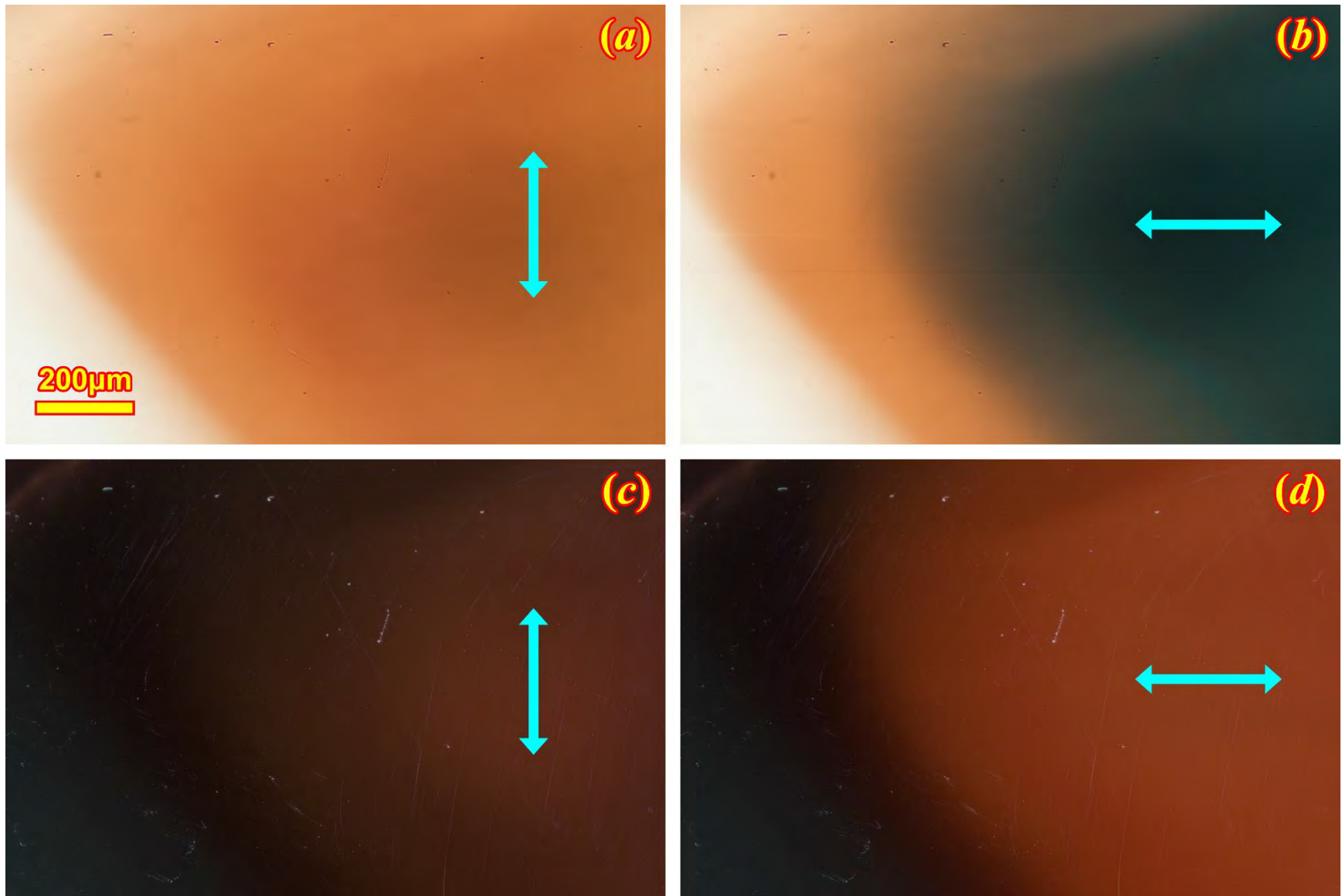
760

761 Figure 9

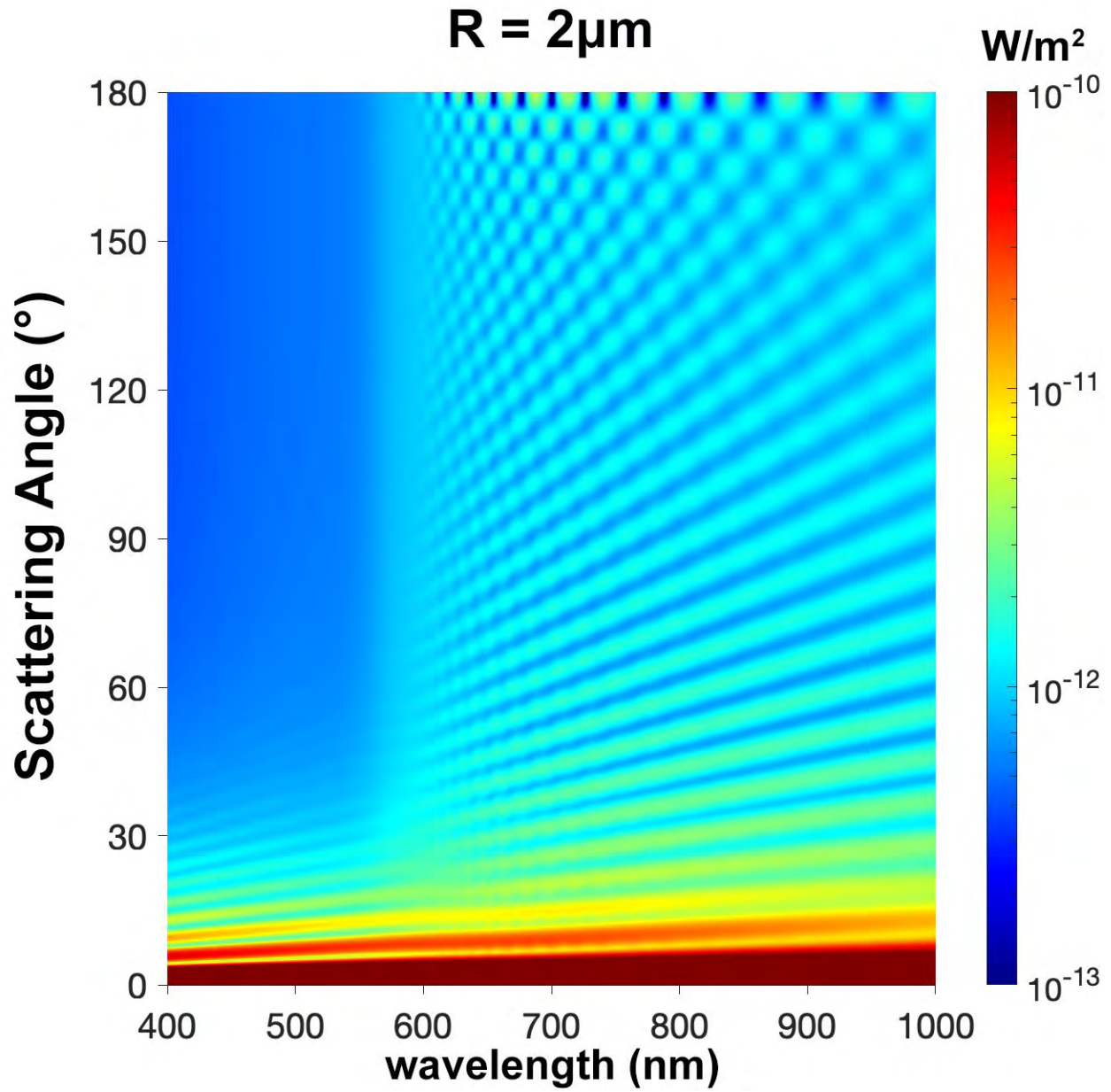


762  
763 Figure 10





764  
765 Figure 11



766  
767 Figure 12  
768