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Sintering-Induced Nucleation and Growth of Noble Metal Nanoparticles for Plasmonic Resonance Ceramic Color

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Abstract

This study demonstrates the formation of nanoparticles (NPs) from metal salts within ceramic glazes, such that the use of this colorant technology is more accessible to artisans, employs less metal content, is less environmentally harmful, and allows for the use of traditional kilns. Gold NPs have been demonstrated to possess a specific, low material loading use as a ceramic glaze colorant via plasmon resonance. Pre-synthesized gold NPs that are added to ceramic glazes have been found to significantly change in size after firing in both reductive and oxidative atmospheres, but still maintain some size relationships and color properties. Unfortunately, it is not viable for the art community to fabricate and employ gold NP systems with high precision in a studio setting; however, the use of noble metal salts or metal oxides are realistic. To that end, this work investigates spontaneous gold and silver NP synthesis by the firing-induced development of NPs from metallic salts included within the glaze materials. Glaze samples with gold and silver salts are fired in reductive and oxidative environments, yielding a range of surface plasmon coloring effects for ceramic coloring. Additionally, the use of gold NP waste (precipitated Au NPs waste) was added to wet ceramic glazes to investigate firing effects on NPs precipitate and potential use as an alternative colorant. Sintering-induced NP nucleation and growth was observed after firing in both oxidation and reduction environments, although to differing degrees. The direct noble metal salt application process eliminates the need for preliminary gold NP synthesis, thus allowing for more practical and environmentally friendly methods in creating plasmonic resonance ceramic coloring, potentially reflective of the processes employed in ancient nanoparticle glasses.

Keywords

ceramics, glazes, gold nanoparticles, silver nanoparticles, firing, salts

1. Introduction

Gold nanoparticles (Au NPs) have a wide range of applications and are common subjects of study in medicine,[1,2] catalysis,[3–5] immunosensors,[6] art,[7,8] and others.[9] Gold has been demonstrated to be an alternative to traditional metal colorants in ceramic glazing, with demonstrated color and up to three orders of magnitude lower metal loading.[10] Traditional glazes use high quantities of metal oxides and carbonates that are often harmful to both the environment and humans.[11,12] Furthermore, high levels of lead- and cadmium-leaching have been observed from traditional ceramic glazes by everyday food products.[13,14] Traditional NP synthesis methods still require many harmful acids and energy-inefficient heating procedures.[15,16] If these steps were eliminated for NP synthesis, a greater ecological advantage could be realized for Au and Ag NP plasmon resonance ceramic color.[17,18]

While Au NPs have been incidentally used since ancient times as colorants in glazes, stained glass,[19] ruby glass,[20] lustreware,[21] Purple of Cassius,[22] enameling,[23] and most famously in the Lycurgus Cup,[24] they have been used primarily as surface inks, lusters, and enamels. Previous studies incorporate tin oxide as an opacifer, brightener, and sacrificial reductant, whereas this study does not.[25,26] This study also explores the effects of firing on precipitated Au NPs (Au NP PPT), essentially the by-product waste material that is produced from fundamental research or industry applications that employ Au NPs.[27–30] By using Au NP waste we are able to not only study the effects of sintering on precipitated Au NPs but also to recycle unwanted lab materials.

The presence of a surface plasmon band for metal NPs allows for an array of versatile optical properties which are dependent on particle size, shape,[31] and produce a wide range of colors.[32] When light strikes the surface of a NP, the surface electrons are excited, and result in an oscillation of electrons around the particle. This oscillation is dependent on the diameter of the particle, such that the relaxation of the electrons allows for a size-dependent color scattering – the plasmon band – that shifts with different NP diameters.[33] Because of the versatility of the plasmon band, metal NPs can be altered for use in a wide variety of different systems that depend on the dimensions and characteristics of the metal NP, which includes orientation,[34] composition,[35] and structure.[36] This phenomenon is most commonly observed for Au NPs with an absorbance around 520 nm for particles with a diameter of ~20 nm (**Fig. 1a and b**) . Silver NPs (Ag NPs) of approximately the same size also demonstrate a surface plasmon band around 410 nm (**Fig. 1c and d**), which has been shown to be useful for applications that are dependent on shape and size.[37,38] While the traditional nucleation processes of NP formation through seeding and growth have been studied and thoroughly understood,[15,16,39] "spontaneous" formation of NPs during both reduction and oxidation sintering has not been previously explored or characterized. Additionally, it is commonly accepted that NP crystals precipitate out of a glaze melt during cooling, resulting in color effects; however, some few works suggest that certain metal NPs undergo nucleation and growth during the heating phase, which can lead to greater control over size parameters and the resulting color properties that are observed.[40,41]

If NP synthesis is no longer required prior to kiln firing, this technology can be immediately adapted to glaze technologies and common practices worldwide. As such, skipping the expensive and tedious steps of traditional NP synthesis can allow one to further eliminate unnecessary economic and environmental stresses with more direct processes. Through a better understanding and further development of these processes, this work offers methodology by which traditional NP synthesis can be eliminated completely in glaze preparation procedures, allowing for cheaper, more ecologically friendly, and more practical glazes for everyday use.

2. Experimental

2.1: Materials

Gold (III) chloride trihydrate (>99.9%) and silver nitrate (>99%) were obtained from Sigma Aldrich. 20 nm Au and Ag NPs were obtained from Ted Pella Inc. Gold precipitate was obtained from in house gold NP waste readily available from other projects in the same laboratory.

2.2: Glaze Synthesis

Glazes consisted of 20% Kaolin EPK, 19% silica, 6% talc, 20% Ferro Frit 3134 (19% CaO, 10% Na_2O, 2% Al_2O_3, 23% B_2O_3, 46% SiO_2), 15% wollastonite, and 20% G-200 feldspar (a stable, borosilicate glaze recipe, stable and vitrified at both cone 6 and 10). 39.38 mg of $HAuCl_4$ and 100 mg of $AgNO_3$ were dissolved in 18.0 MΩ·cm nanopure water in 20 g scintillation vials. The aluminum seals were removed from the scintillation caps before adding the metal salts. The salt solutions were then added to 160 g and 200g glaze batches, respectively. In an effort to further reduce waste, we observed the effects of firing on precipitated Au nanoparticle waste (Au NP PPT) that was collected from previous experiments in our own lab to create new, vibrant glazes without rendering more waste (**Fig. 2a and b**). The Au NP PPT waste solution consisted of severely precipitated citrate- and thioalkane-stabilized Au NPs from other experiments [10,42–44]that settled leaving a clear supernatant. A UV-vis spectrum was taken of a diluted sample of the Au NP PPT solution that was agitated to suspend the precipitate in solution. The spectrum shows that the Au NP PPT was so severely aggregated and precipitated that there is no visible absorbance band from the plasmon band (**Fig. 2b inset**). By incorporating the Au NP PPT waste into glazes, we are able to observe the NP color after firing. Purchased Ag NPs with diameter sizes of 21.5 ± 4.9 nm were used with glaze samples as a stock reference (**Figure 1d**). Roughly 10 mL of Au NP PPT was added to a 200 g glaze batch. 5 mL of silver NP solution was added to an 80 g glaze batch. Ceramic samples were then dipped in each glaze and fired in both reductive and oxidative kilns at cones 10 (1285 ºC, 2345 ºF) and 6 (1200 ºC, 2200 ºF), respectively.

2.3: Post-Firing Glaze Analysis

After samples were fired, glaze from the back of each sample was ground using a Dremel, and the glaze dust was collected in separate vials. The glaze dust was then processed with a mortar and pestle for several minutes or once the glaze turned into a fine powder. The powder was then returned to the vial and suspended in ethanol. The mortar and pestle were rinsed with ethanol and water between samples. A 5.0 μL volume of each solution was then deposited on 400-grid, carbon-coated, mesh TEM grids and analyzed. At least 100 NPs were measured for each sample to calculate average NP diameters.

2.4: Firing

For samples that were fired in a reduction atmosphere, the reduction kiln was slowly heated over twelve hours. Upon reaching 1000°F (538ºC), the kiln was then heated up to cone 10 at 2345°F (1285ºC) over eight hours. After firing, the kiln was allowed to cool for 24 hours, and then the samples were removed for analysis. The oxidation samples were fired in Nichrome wire kilns to cone 6 (1200 ºC, 2200 ºF) on a medium setting. Air was slowly pulled through the kiln via a venting mechanism, which contributes to the oxidative atmosphere. The kiln was then allowed to cool for 24 hours before removing the samples. For both reductive and oxidative kilns, the samples were fired alongside other normal pottery at the Visual Arts Center of Richmond. This is significant to demonstrate the ease of this application for use by craft artists and without the need for special synthesis equipment.

Reflectance spectra measurements were taken for all samples, indicative of glaze color quality and intensity, using an Ocean Optics Halogen lamp (HL-2000-FHSA) and Flame miniature spectrometer (FLAME-S-VIS-NIR-ES, 350-1000 nm).

3: Results and Discussion

A range of NP glazes were tested in both common reductive and oxidative firing conditions, and the results examined for color and particle size distributions.

3.1: Nanoparticle Color and Sizes after Firing

NP formation was observed in all four glaze types – $HAuCl_4$, $AgNO_3$, Au NP PPT, and Ag NPs – in both firing conditions (reduction and oxidation). The reduction-fired $HAuCl_4$ glaze (**Fig. 3a**, **left sample**) exhibits a dark red-purple color – a result suggesting the presence of Au NPs in the gold salt-based glaze. The oxidized-fired sample (**Fig. 3a**, **right sample**) yielded a light pink color for oxidation environments. These color profiles are consistent with those first synthesized by Lambertson et al. From TEM analysis (shown in **Fig. 3a**), the reduced and oxidized $HAuCl_4$ glazes produced average NP sizes of 25.0 ± 13.0 nm and 38.5 ± 7.9 nm, respectively. When $AgNO_3$ is included in the pre-fired glaze mixture and fired in a reductive environment, the resulting glaze is a burnt laurel green (**Fig. 3b**, **left sample**) with an average NP size of 12.2 ± 4.0 nm. The oxidized $AgNO_3$ sample (**Fig. 3b**, **right sample**) resulted in a very light white-green color with NP size of 21.0 ± 11.0 nm. This color is consistent with previous studies involving Ag NPs to produce a green color.[45,46] When Au NP PPT is a component of the glaze (**Fig. 3c**, **left**

sample) in a reduction firing, a light red-brown color was observed, and the oxidized sample (**Fig. 3c**, **right sample**) resulted in an orange glaze with average NP sizes of 21.2 ± 14.3 nm and 40.4 ± 10.7 nm, respectively. Reduction-fired Ag NP (**Fig. 3d**, **left sample**) produced a light jade color with average NP size of 4.3 ± 2.4 nm, while the oxidized sample (**Fig. 3d**, **right sample**) yielded almost no color with NP size analysis of 13.4 ± 4.8. As confirmed with TEM analysis, all eight samples possess some NP formation, suggestive of NP formation during heating**.** Both individual Au NPs and precipitated Au NPs were observed in the reduction glaze sample of Au NP PPT, which would suggest renucleation and growth during firing. Fired tile samples were broken in half to show cross-sectional profiles of all four glaze types (**Fig. 4**). The cross sections show that the NPs are held within a suspension system with colors permeating throughout the glaze as opposed to residing purely on the surface. All glaze colors in **Fig. 4** correspond to the same tiles shown in **Fig. 3**.

For reduction-fired samples, incomplete gas combustion in the kiln, and resulting carbon monoxide (CO), are responsible for a reductive flow of elections into ceramic surfaces, **Scheme 1**.[47,48] This mechanism can allow for the reduction of Au or Ag atoms via nucleation, growth, and formation of suspended NPs, not just precipitation of material colorants from the glaze during cooling. Surprisingly, NPs are present in oxidation-fired glazes, even though samples were prepared with cationic noble metal salts of Au^{3+} and Ag^{+}(**Fig. 3a and b**). In an oxidative environment, the charged metal salt undergoes some amount of reduction, nucleates, undergoes growth, and ultimately results in stable NPs, **Scheme 2**. This suggests the presence of getter reduction in the glaze. Through this mechanism, the "getter" acts as a sacrificial molecule or atom in giving up electrons to the metal salt, forming the initial nucleation and growth of NPs during heating.[49] Impurities that exist within the clay or glaze may act as the getter, which would allow for a weak but still visible presence of reduction and formation of NPs, consistent with earlier studies.[50] The same phenomenon could occur for Au precipitate (**Figure 3c**). The presence of an oxidative atmosphere potentially inhibits re-nucleation and growth of degraded particles that are lost to heat, thus the particle diameter averages are larger. Precipitated NPs are observed to remain in the glaze alongside newly formed NPs. Analysis of the TEM imaging from the stock Ag NPs samples indicates similar behavior to the Au NPs after both reductive and oxidative firing (**Fig. 3d**).

3.2: Color Profile Quantification

As an effect of surface plasmon resonance for both Au and Ag NPs within glazes, color intensity and quality can be used to complement imaging techniques and sizing analysis results to build a more complete understanding of glaze composition. Thus, as the number of NPs increases within a glaze profile, the color becomes deeper and results in a lower percent reflectance in other parts of the visible spectrum. Percent reflectance spectra demonstrate a reciprocal relationship between reflectance and color brightness;[51] more vibrant, deep colors demonstrate a net lower percent reflectance, whereas lighter, more pale colors are observed to have a higher percent reflectance profile across the visible spectrum. Surprisingly, though $HAuCl_4$ and Au NP PPT both contain gold, the $HAuCl_4$ precursor glaze samples demonstrate a lower percent reflectance (and thus a more vibrant color) than the reduction-fired Au NP PPT glaze sample; reciprocally, the oxidized sample of $HAuCl_4$ is observed to possess a higher percent reflectance and is lighter in color than that of Au NP PPT. For the Ag samples, those fired in reduction significantly differ between the $AgNO_3$ and Ag NP tiles (**Fig. 3c and d, left**). The reduction-fired $AgNO_3$ glazes produced a burnt laurel green whereas the reduced Ag NP produced a light jade green-blue. This difference can also be seen in the reflectance spectra graphs in **Fig. 5b and 5d**. The significant difference between the reductive and oxidative reflectance spectra for the $AgNO_3$ samples are a function of the differences in color – from the laurel green to the white (**Fig. 5b**). Both oxidation-fired silver samples resulted in very pale, consistent results with minimal color. Reduction-fired Ag NPs glaze samples resulted in a vibrant glaze that contained smaller but more plentiful NPs (deeper color and lower % reflectance measurements). Oxidized Ag NPs resulted in a pale, almost translucent glaze with larger but fewer (higher % reflectance) NPs.

3.3: Sizing Comparison

Sizing trends of the four glaze systems are consistent between the reductive and oxidative samples as shown in **Fig. 6**. An oxidative firing atmosphere yields larger average NP sizes than those of a reductive firing atmosphere. This trend is consistent with previous work and suggestive that a higher temperature, reductive atmosphere may contribute to greater particle degradation as a result of greater heat work. For all four glazes from different metal salt precursors, the oxidized samples yielded NPs that were significantly larger than their respective reduced sample equivalent: +35% for $HAuCl_4$, +42% for $AgNO_3$, +47% for Au NP PPT, and +68% for Ag NPs (**Fig. 6**). To that end, a reductive atmosphere could also lead to the production of new, smaller NPs through promoting nucleation and regrowth.[25] This would shift the average particle diameter to be somewhat smaller while also displaying more plentiful NPs and deeper color. Alternatively, an oxidative atmosphere only promotes weaker getter reduction with less heat work degradation, which would yield larger but fewer NPs. Both of these phenomena occur regardless of noble metal and starting state of the metal across all samples. The stock Ag NPs have a fairly uniform starting size (21.5 ± 4.9 nm) and thus have relatively small standard deviations in both reduction-fired and oxidation-fired samples. There is overlap of the error bars, but there are significant differences in average diameters among the samples (**Fig. 6**). These size trends are supportive of the possible degradation/growth mechanisms proposed above based on the difference in firing atmospheres and in previous studies;[10,50] however, new studies are currently being developed to further elucidate these processes.

4. Conclusion

This study explores the sintering-induced formation of nanoparticles in ceramic glazes among reductive and oxidative kilns to produce a wide variety of colors. Directly adding the metal salts $HAuCl_4$ or $AgNO_3$ to glazes allows for the formation of gold and silver nanoparticles during both reduction and oxidation firing processes. Gold precipitate is also observed to degrade and renucleate into new gold nanoparticles alongside precipitated materials. This allows for comparable color profiles to traditional red glazes and previously reported new gold nanoparticle glazes by recycling nanoparticle synthesis waste. The data presented in this study introduces new methods by which noble metal salts may be employed alongside modern glazes for natural nanoparticle nucleation and growth during firing, resulting in low metal loading plasmon resonance coloring. These methods bypass preliminary NP synthesis that require atypical acids, solvents, heat, precision, and equipment that artisans seldom possess. This work provides valuable insight and realistic parameters that are suggestive of the original processes employed by ancient artisans to create noble metal nanoparticle glasses and glazes, while introducing new methods for creating vibrant glazes from noble metals that are easy, cost-effective, and environmentally friendly. Finally, these glazes can be prepared and fired alongside traditional glazes without costly scientific instruments or precision for use by everyday artists.

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REFERENCES

1. D. A. Giljohann, D. S. Seferos, W. L. Daniel, M. D. Massich, P. C. Patel, and C. A. Mirkin, Angew. Chem. Int. Ed Engl. **49**, 3280 (2010).

2. L. Zhang, F. X. Gu, J. M. Chan, A. Z. Wang, R. S. Langer, and O. C. Farokhzad, Clin. Pharmacol. Ther. **83**, 761 (2008).

3. N. Lopez and J. K. Nørskov, J. Am. Chem. Soc. **124**, 11262 (2002).

4. T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, and K. Kaneda, Adv. Synth. Catal. **351**, 1890 (2009).

5. Q. Yang, Q. Xu, and H.-L. Jiang, Chem. Soc. Rev. **46**, 4774 (2017).

6. V. C. Rodrigues, M. L. Moraes, J. C. Soares, A. C. Soares, R. Sanfelice, E. Deffune, and O. N. Oliveira, Bull. Chem. Soc. Jpn. **91**, 891 (2018).

7. C. J. Murphy, Science **298**, 2139 (2002).

8. L. Catherine and P. Olivier, *Gold Nanoparticles For Physics, Chemistry And Biology (Second Edition)* (World Scientific, 2017).

9. I. Chakraborty and T. Pradeep, Chem. Rev. **117**, 8208 (2017).

10. R. H. Lambertson, C. A. Lacy, S. D. Gillespie, M. C. Leopold, and R. H. Coppage, J. Am. Ceram. Soc. **100**, 3943 (2017).

11. S. Satarug and M. R. Moore, Environ. Health Perspect. **112**, 1099 (2004).

12. T. A. Aderemi, A. A. Adenuga, J. A. O. Oyekunle, and A. O. Ogunfowokan, Environ. Sci. Pollut. Res. **24**, 17116 (2017).

13. R. W. Sheets, Sci. Total Environ. **197**, 167 (1997).

14. M. I. Ahmad, S. Abdelfatah, and S. Al-Meer, Int. J. Public Health Res. **5**, 13 (2017).

15. J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, and A. Plech, J. Phys. Chem. B **110**, 15700 (2006).

16. N. R. Jana, L. Gearheart, and C. J. Murphy, Langmuir **17**, 6782 (2001).

17. P. Colomban, A. Tournié, and P. Ricciardi, J. Raman Spectrosc. **40**, 1949 (2009).

18. F. Drünert, M. Blanz, K. Pollok, Z. Pan, L. Wondraczek, and D. Möncke, Opt. Mater. **76**, 375 (2018).

19. O. Schalm, V. Van der Linden, P. Frederickx, S. Luyten, G. Van der Snickt, J. Caen, D. Schryvers, K. Janssens, E. Cornelis, D. Van Dyck, and M. Schreiner, Spectrochim. Acta Part B At. Spectrosc. **64**, 812 (2009).

20. A. Ruivo, C. Gomes, A. Lima, M. L. Botelho, R. Melo, A. Belchior, and A. Pires de Matos, J. Cult. Herit. **9**, e134 (2008).

21. P. Sciau, Deliv. Nanoparticles (2012).

22. Christopher Corti and Richard Holliday, in *Gold Sci. Appl.* (Taylor & Francis Group, Boca Raton, 2010), pp. 350–357.

23. J. Carbert, Gold Bull. **13**, 144 (1980).

24. I. Freestone, N. Meeks, M. Sax, and C. Higgitt, Gold Bull. **40**, 270 (2007).

25. S. Haslbeck, K.-P. Martinek, L. Stievano, and F. E. Wagner, in *ICAME 2005*, edited by P.-E. Lippens, J.-C. Jumas, and J.-M. R. Génin (Springer Berlin Heidelberg, 2007), pp. 89–94.

26. F. Springer, in *Ind. Ceram.* (Chapman & Hall, 1963), pp. 647–650.

27. A. S. K. Hashmi and G. J. Hutchings, Angew. Chem. Int. Ed. **45**, 7896 (2006).

28. S. Carrettin, M. C. Blanco, A. Corma, and A. S. K. Hashmi, Adv. Synth. Catal. **348**, 1283 (2006).

29. M. C. Leopold, T. T. Doan, M. J. Mullaney, A. F. Loftus, and C. M. Kidd, J. Appl. Electrochem. **45**, 1069 (2015).

30. M. B. Wayu, M. J. Pannell, and M. C. Leopold, ChemElectroChem **3**, 1245 (2016).

31. T. A. El-Brolossy, T. Abdallah, M. B. Mohamed, S. Abdallah, K. Easawi, S. Negm, and H. Talaat, Eur. Phys. J. Spec. Top. **153**, 361 (2008).

32. X. Huang and M. A. El-Sayed, J. Adv. Res. **1**, 13 (2010).

33. W. Haiss, N. T. K. Thanh, J. Aveyard, and D. G. Fernig, Anal. Chem. **79**, 4215 (2007).

34. J. Vieaud, J. Gao, J. Cane, M. Stchakovsky, A. En Naciri, K. Ariga, R. Oda, E. Pouget, and Y. Battie, J. Phys. Chem. C **122**, 11973 (2018).

35. H. Shirai, M. T. Nguyen, D. Čempel, H. Tsukamoto, T. Tokunaga, Y.-C. Liao, and T. Yonezawa, Bull. Chem. Soc. Jpn. **90**, 279 (2016).

36. K. K. R. Datta, B. V. S. Reddy, K. Ariga, and A. Vinu, Angew. Chem. Int. Ed. **49**, 5961 (2010).

37. D. D. Evanoff and G. Chumanov, ChemPhysChem **6**, 1221 (2005).

38. A. L. González, C. Noguez, J. Beránek, and A. S. Barnard, J. Phys. Chem. C **118**, 9128 (2014).

39. A. Gole and C. J. Murphy, Chem. Mater. **16**, 3633 (2004).

40. B. Karasu and S. Turan, J. Eur. Ceram. Soc. **22**, 1447 (2002).

41. N. V. Rudkovskaya and N. Y. Mikhailenko, Glass Ceram. **58**, 387 (2001).

42. A. R. Schmidt, N. D. T. Nguyen, and M. C. Leopold, Langmuir **29**, 4574 (2013).

43. T. T. Doan, R. W. Day, and M. C. Leopold, J. Mater. Sci. **47**, 108 (2012).

44. C. E. Dowdy and M. C. Leopold, Thin Solid Films **519**, 790 (2010).

45. J. Ueda, M. Samusawa, K. Kumagai, A. Ishida, and S. Tanabe, J. Mater. Sci. **49**, 3299 (2014).

46. R. Yu, P. Mazumder, N. F. Borrelli, A. Carrilero, D. S. Ghosh, R. A. Maniyara, D. Baker, F. J. García de Abajo, and V. Pruneri, ACS Photonics **3**, 1194 (2016).

47. B. Carter and G. Norton, in *Ceram. Mater. Sci. Eng.* (Springer, New York, 2013), pp. 144–145.

48. J Hirschhorn, *Introduction to Powder Metallurgy* (American Powder Metallurgy Institute, New York, 1969).

49. Werner Espe, Max Knoll, and Marshall P. Wilder, Electronics (1950).

50. N. N. Dinh, L. T. DiPasquale, M. C. Leopold, and R. H. Coppage, Gold Bull. 1 (2018).

51. Paul M. Whitmore and Catherine Baile, J. Am. Institude Conserv. **36**, 207 (1997).