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Boiling-induced formation of colloidal gold in black smoker hydrothermal fluids

Amy Gartman[1], Mark Hannington[2,3], John W. Jamieson[4], Ben Peterkin[4], Dieter Garbe-Schönberg[5], Alyssa J. Findlay[6]*, Sebastian Fuchs[2], and Tom Kwasnitschka[2]

[1]U.S. Geological Survey Pacific Coastal and Marine Science Center, 2885 Mission Street, Santa Cruz, California 95060, USA
[2]GEOMAR–Helmholtz Centre for Ocean Research Kiel, 1-3 Wischhofstrasse, 24148 Kiel, Germany
[3]Department of Earth Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada
[4]Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X5, Canada
[5]Institute of Geosciences, Kiel University, Ludewig-Meyn-Strasse 10, 24118 Kiel, Germany
[6]Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

ABSTRACT

Gold colloids occur in black smoker fluids from the Niua South hydrothermal vent field, Lau Basin (South Pacific Ocean), confirming the long-standing hypothesis that gold may undergo colloidal transport in hydrothermal fluids. Six black smoker vents, varying in temperature from 250 °C to 325 °C, were sampled; the 325 °C vent was boiling at the time of sampling and the 250 °C fluids were diffusely venting. Native gold particles ranging from <50 nm to 2 μm were identified in 4 of the fluid samples and were also observed to precipitate on the sampler during collection from the boiling vent. Total gold concentrations (dissolved and particulate) in the fluid samples range from 1.6 to 5.4 nM in the high-temperature, focused flow vents. Although the gold concentrations in the focused flow fluids are relatively high, they are lower than potential solubilities prior to boiling and indicate that precipitation was boiling induced, with sulfide lost upon boiling to exsolution and metal sulfide formation. Gold concentrations reach 26.7 nM in the 250 °C diffuse flow sample, and abundant native gold particles were also found in the fluids and associated sulfide chimney and are interpreted to be a product of colloid accumulation and growth following initial precipitation upon boiling. These results indicate that colloid-driven precipitation as a result of boiling, the persistence of colloids after boiling, and the accumulation of colloids in diffuse flow fluids are important mechanisms for the enrichment of gold in seafloor hydrothermal systems.

INTRODUCTION

Boiling has long been recognized as an effective mechanism for depositing precious metals from solution, including as scales in geothermal wells (Drummond and Ohmoto, 1985; Brown, 1986; Spycher and Reed, 1989; Clark and Williams-Jones, 1990; Simmons and Browne, 2000). In terrestrial epithermal deposits, where boiling may also contribute to metal loss from solution (Simmons et al., 2016), gold, silver, and other elements coprecipitate with colloidal sulfides, related to the transport of gold as sulfide species in these fluids (Pope et al., 2005). However, gold-depositing processes, specifically the precipitation of discrete gold colloids, have not been observed directly. The first experimental evidence for the stability of gold colloids in hydrothermal systems was obtained nearly 80 years ago (Frondel, 1938), but there has been little agreement about the role of these colloids in ore formation (Saunders, 1990; Herrington and Wilkinson, 1993; Saunders and Schoenly, 1995; Williams-Jones et al., 2009; Saunders et al., 2010, 2014). Instead, experimental studies of gold in high-temperature hydrothermal fluids have focused on aqueous species, with sulfide as the major ligand complexing Au in solution under conditions typical of black smoker fluids similar to those considered here (e.g., Benning and Seward, 1996; Stefánsson and Seward, 2004). Under such conditions, cooling and oxidation occur as a result of hydrothermal fluid–seawater mixing and may result in gold precipitation, sometimes producing native gold in hydrothermal chimneys (Herzig et al., 1993; Hannington et al., 1995; Moss and Scott, 2001, Törmänen and Koski, 2006). In this paper we describe the first occurrence of colloidal gold in fluids from actively boiling hydrothermal vents in the Lau Basin (South Pacific Ocean). We present evidence that gold colloids form as a result of boiling, and that a fraction of the colloidal gold escapes deposition at the boiling horizon and continues to be transported with the rising fluids, explaining the high concentrations of gold in all of the chimney samples and suggesting that colloids may be an important transport mechanism for gold throughout aqueous ore-forming systems.

LOCATION AND METHODS

The sampled vents occur on Niua South, the southern of two volcanic cones that make up the Niua Volcano, at the northern termination of the Tonga volcanic arc (15.164°S, 173.757°W; Fig. DR1 in the GSA Data Repository[1]; Resing et al., 2011). High-temperature hydrothermal venting is restricted to the floor of a 500-m-diameter crater on the eastern flank of Niua South, where dozens of active vents occur within an area of 150 × 200 m. The vents compose low mounds of massive sulfide capped by 1–5-m-tall sulfide chimneys composed mainly of pyrite, sphalerite, chalcopyrite, barite, and anhydrite. The deepest black smoker vents occur at a depth of 1164 m, have a maximum recorded temperature of 325 °C, and are actively boiling (Fig. 1A).

Hydrothermal fluid samples were collected from six sites by the remotely operated vehicle (ROV) ROPOS, using titanium major samplers (750 mL). Prior to sampling, the temperature of the orifice was measured using the high-temperature probe on the ROV. Four of the six sites were sampled in duplicate. Samples were processed immediately upon shipboard recovery, at which point the temperature and pH of the fluids were also recorded. Separate aliquots of the whole (i.e., unfiltered) fluid were taken for measurement of major and trace elements, as well as acid volatile sulfide and chromium reducible sulfide. Because the fluids were

*Current Address: Center for Geomicrobiology, Department of Biological Sciences, Aarhus University, 8000 Aarhus C, Denmark.

[1]GSA Data Repository item 2018008, Figure DR1 (map of Niua), Figure DR2 (photograph of the tarnish that developed during sampling), Figure DR3 (additional SEM/EDS), Figure DR4 (temperature, pressure, and boiling of fluids at Niua), Figure DR5 (calculated solubilities for Au at Niua). and Table DR1 (fluid concentration and location of fluid collection), is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.

Figure 1. Photographs of types of fluid emission. Left to right: boiling hydrothermal fluid, focused flow fluid, diffuse flow fluid. Snorkel nozzle is ½" diameter.

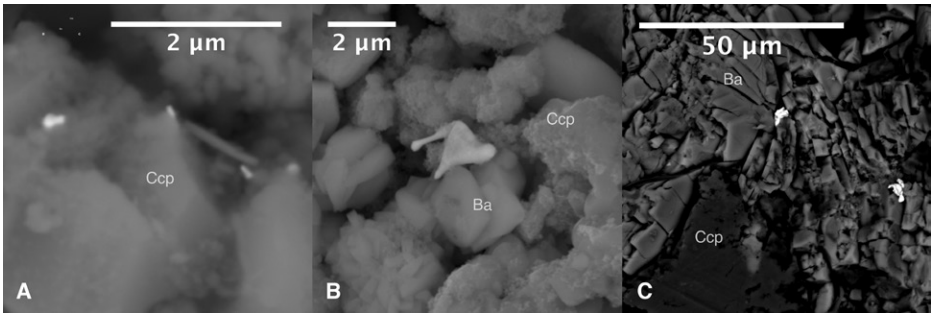

Figure 2. Scanning electron microscopy of representative Au particles. Minerals surrounding the gold are labeled. Ccp—chalcopyrite; Ba—barite. A: Collected from focused flow fluids. B: Collected from diffuse flow fluids. C: From the diffuse flow chimney.

unfiltered, larger particles (>0.2 µm) may also have been present in the fluids. For major elements, samples were acidified with HCl to below pH 1 and were further leached upon return to shore with nitric acid prior to analysis by inductively coupled plasma–mass spectrometry.

Following subsampling of the liquid, the remaining fluid was spun down using a shipboard centrifuge (Gartman et al., 2014). The resulting pellet was then capped with N_2 and frozen at –20 °C. In the laboratory, the frozen pellets were resuspended in Mill-Q water and evaporated directly onto aluminum stubs for scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) analysis on a Tescan VP-SEM in high vacuum mode, without conductive coating. Imaging was performed using both secondary electron and backscatter detectors, and particle dimensions were measured using ImageJ (https://imagej.net/) software. Samples of the chimney walls collected at the vent orifice were examined using an FEI (https://www.fei.com) MLA (mineral liberation analyzer) 650F SEM under high vacuum and also analyzed for bulk Au content by instrumental neutron activation analysis. Additional details of the sampling and analytical methods used for the fluids, particles, and chimney samples are provided in the Data Repository.

FLUID, PARTICULATE, AND CHIMNEY GOLD

Gold particles ranging in size from <50 nm to 2 µm were found in both focused and diffuse flow fluids at Niua, as well as on a black tarnish, mainly composed of metal sulfide minerals, that developed on the exterior of the snorkel during sampling of the boiling vent (Fig. 1; Fig. DR2). The majority of particles have anhedral shapes ranging from round (n = 18) to oblong (n = 14), with average dimensions of 0.44 × 0.31 µm (median 0.33 × 0.20 µm). Almost all (95%) particles had at least one dimension that was shorter than 1 µm; 29% of the particles exhibit a dimension of <100 nm and can be considered nanoparticles (Fig. 2A). The majority of larger (>500 nm) particles appear discrete and likely result from particle growth (Fig. 2B; Fig. DR3), although apparent colloidal aggregates are also present (Fig. 2A). Chalcopyrite and barite were also present in the fluids, and two of the gold particles are embedded in barite. The majority of Au particles appear to be native Au with Ag levels below the detection limits of EDS, with the exception of 4 particles containing Ag between 4.6 and 6.9 mol% (2.5–3.8 wt%) relative to Au.

Gold particles were also found in sulfides from the wall of the diffusely venting chimney; two of the particles are <1 µm in size, the other four are larger (2–5 µm) than any particles found in the fluids (Figs. 2C and 3). Chimney samples from the focused flow and boiling vents contain an average of 6 mg/kg of Au (ranging from 3.6 to 11.4 mg/kg, n = 5; Table DR1). A sample from the diffusely venting chimney contains >30 mg/kg Au. Like the Au in the fluid, these particles are associated with chalcopyrite and barite.

Gold concentrations in the fluid samples (unfiltered fluids, which include dissolved and particulate gold) range from 3.1 to 3.7 nM in the boiling vents, and 1.6–5.4 nM in the focused flow vents (Table DR1). The number of gold particles observed in the samples from the focused flow fluids (n = 6, 3, and 1) correlates generally with the bulk gold concentrations (3.1 nM, 2.0 nM, and 1.6 nM, respectively; Fig. 4); mass balance calculations relating the amount of gold present in particles to the amount of gold measured in fluids suggest that most of the gold is present as colloids. The diffuse fluid sample, which contains the most (n = 25) and the

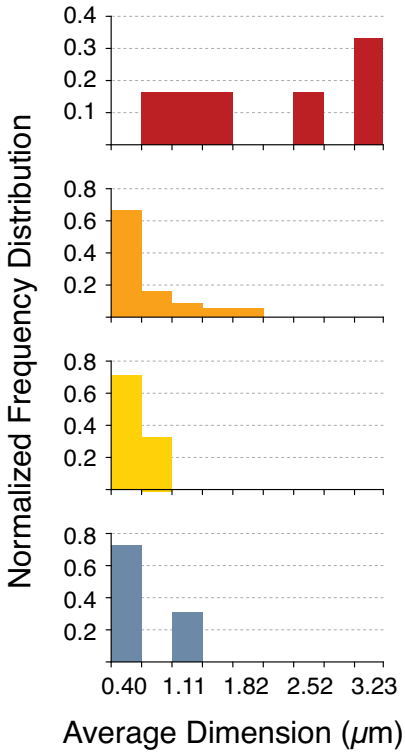

Figure 3. Histogram of average dimensions of particles observed using scanning electron microscopy. From top to bottom: in the chimney piece corresponding to the diffuse flow sample (n = 6); in the diffuse flow fluids (n = 25); in the focused flow fluids (n = 10); on the deposit formed on the sampler nozzle (n = 7).

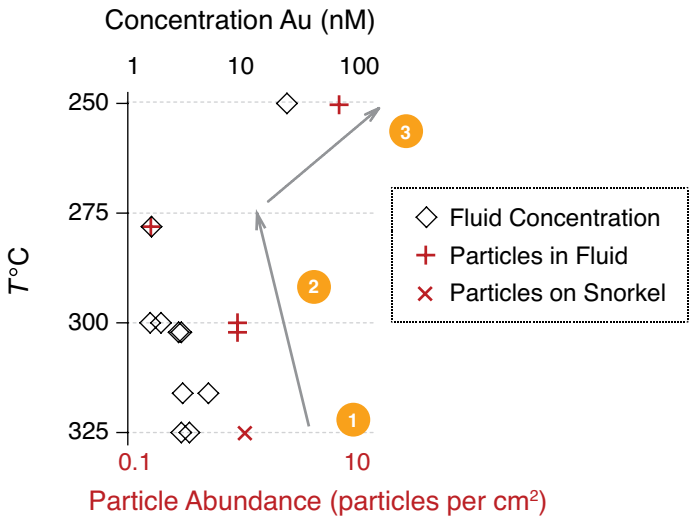

Figure 4. Temperature (*T*) versus gold for fluids at Niua, Lau Basin, South Pacific Ocean. The x-axes are log scale. Gold concentrations in the fluids are plotted as black diamonds; error is much smaller than the size of the data point. The number of Au particles identified is plotted in red; x refers to particles found in the snorkel tarnish, plus sign refers to particles found in the fluid. (1) Au precipitates from solution upon boiling, forming colloids. (2) The Au colloids formed upon boiling are transported with the fluids. As the fluids cool, colloids are gradually lost from solution. (3) In low-temperature diffuse flow zones, colloid growth and settling exceed emission, resulting in gold accumulation in the fluids followed by deposition in the sulfide chimney.

largest gold particles, has the highest bulk Au concentration (26.7 nM) of the analyzed samples.

FORMATION OF COLLOIDAL GOLD

The highest temperature sample was both visibly boiling and plots directly on the seawater boiling curve (Fig. DR4). At Niua, the solubility of gold under pre-boiling conditions is ~10× higher than the concentration in focused flow fluids that were collected after boiling (Fig. DR5). However, sulfide loss at the point of boiling due to both vaporization and the observed precipitation of metal sulfides could have resulted in fluid supersaturation with gold carried originally as either $Au(HS)_2^-$ and $AuHS^0$, resulting in the rapid nucleation of colloidal gold particles (e.g., Saunders and Schoenly, 1995). The concentrations of sulfide measured here are low (Table DR1), consistent with loss upon boiling. Gold concentrations in the vent fluids at Niua do not correlate with Mg, a measure of seawater–hydrothermal fluid mixing, consistent with the gold transport in fluids being dominated by particles rather than dissolved species.

Deposition of colloidal gold at the point of boiling was observed on the black tarnish that precipitated on the sampler snorkel (Fig. DR2), and high concentrations of gold were present in the corresponding chimney sample, although no gold particles were observed in the chimney or the boiling fluids. It is probable that the initial gold colloids that form upon boiling are smaller than we could observe with SEM, as initial gold nanoparticles precipitated via common boiling syntheses often range from 1 to 20 nm (Daniel and Astruc, 2004). The particles that occur in the focused flow fluids, diffuse fluids, and chimney wall, in which irregularity of shape increases with size, are consistent with particle growth after boiling-induced nucleation (Figs. 3 and 4).

Indirect evidence of solid precious metal nanoparticles in fluid inclusions from epithermal veins (Kouzmanov et al., 2010) and isotopic evidence (Saunders et al., 2016) present the possibility that in some systems, gold particles may exist in the fluids even prior to boiling. This process may be particularly common at arc volcanoes where hydrothermal fluids are pre-enriched in gold and other elements as a result of magmatic volatile input (Hedenquist and Lowenstern, 1994; de Ronde et al., 2011; Berkenbosch et al., 2012; Schmidt et al., 2017). However, at Niua, the formation of gold particles on the snorkel tarnish, the elevated concentration of gold in the boiled chimney, the undersaturation of Au in pre-boiled fluids (Fig. DR5), and the transport of particulate gold in boiling, focused, and diffuse flow fluids, suggest that the precipitation at Niua is boiling induced, as previously suggested for bonanza Au-Ag precious metal vein mineralization at the Sleeper deposit in Nevada (Saunders and Schoenly, 1995) and in gold-supersaturated seawater-dominated fluids in the Reykjanes (Iceland) geothermal field (Hannington et al., 2016).

CONCLUSIONS

The occurrence of gold colloids in hydrothermal fluids of the Niua vent field indicates a process by which gold is initially precipitated in high-temperature boiling fluids and subsequently transported in particulate form into lower temperature vents (Fig. 4). At depth, before the hydrothermal fluids reach the seafloor, gold is most likely present in solution, as suggested by solubility calculations (Fig. DR5). Boiling, and the rapid loss of sulfide to exsolution and to the formation of metal sulfides, induces gold precipitation as colloids. Some of the colloidal gold adheres to local chimney walls, and the remainder is carried upward in suspension, potentially stabilized by capping agents present in hydrothermal fluids (e.g., thiols; Reeves et al., 2014). As the fluids cool (Fig. 4), the colloids aggregate and grow, with some additional loss from suspension. At the lowest temperature site, the fluid is diffusely vented, resulting in particle settling that is more rapid than particle outflow and concentration of the gold colloids and particles within the diffusely venting fluids. Diffuse venting in white smokers has long been linked to gold enrichment due to mixing and cooling of the hydrothermal fluids and associated loss of aqueous sulfur complexes (Hannington et al., 1986). The observations at Niua suggest an important alternative mechanism for gold transport into the low-temperature vents.

The presence of colloidal gold particles in hydrothermal fluids and sulfide chimneys at Niua South has several implications for the formation of Au-rich ore deposits: it confirms a nearly 80-yr-old hypothesis that Au can be transported colloidally in geothermal solutions, further demonstrates that Au colloids can remain suspended after boiling, and shows that the accumulation of colloids in boiled liquids can eventually result in gold concentrations that exceed saturation values. These findings provide direct observational insight into the role that colloids may play in high-grade gold mineralization, especially at seafloor massive sulfide deposits.

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