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Gold enrichment in active geothermal systems by accumulating colloidal suspensions

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The origins of high-grade hydrothermal ore deposits are debated, but active geothermal systems provide important clues to their formation[1,2]. The highest concentrations of gold are found in geothermal systems with direct links to island arc magmatism[3–7]. Yet, similar concentrations have also been found in the absence of any input from arc magmas, for example, in the Reykjanes geothermal field, Iceland[8]. Here we analyse brine samples taken from deep wells at Reykjanes and find that gold concentrations in the reservoir zone have increased over the past seven years from an average of 3 ppb to 14 ppb. The metal concentrations greatly exceed the maximum solubility of gold in the reservoir under saturated conditions and are now nearly two orders of magnitude higher than in mid-ocean ridge black smoker fluids—the direct analogues of Reykjanes deep liquids[8,9]. We suggest that ongoing extraction of brine, the resulting pressure drop, and increased boiling have caused gold to drop out of solution and become trapped in the reservoir as a colloidal suspension. This process may explain how the stock of metal in the reservoirs of fossil geothermal systems could have increased over time and thus become available for the formation of gold-rich ore deposits.

The studied geothermal wells are located <20 m above sea level on the Reykjanes Peninsula (Fig. 1). They differ from other geothermal production systems on Iceland because the liquid harnessed for electrical power generation is modified sea water[8]. The fluid reservoir is situated between 1,000 and 2,800 m below the surface, and measured temperatures at these depths range from 270 to 315 °C (refs 8,10). At the surface, geothermal features cover an area of ~1 km^2, but the thermal anomaly at depth is at least 2 km in diameter, indicated by a large resistivity low at depth that encompasses nearly the entire width of the peninsula[10]. The reservoir rocks are basaltic lava flows with mid-ocean-ridge basalt-like compositions, together with tuffaceous sediment, and hyaloclastite; dykes increase in abundance with depth[11]. High-temperature fluids that are feeding the reservoir at ~100 kg s^{-1} (ref. 12) have a salinity of ~3.2 wt% NaCl and a pH of 5 to 6, closely resembling seawater-derived black smoker fluids from mid-ocean ridge hot springs[8]. Oxygen and hydrogen isotope data show little or no evidence of a magmatic input[13], unlike systems associated with arc magmas[4], and there is virtually no mixing with surface water[13,14]. Boiling of the deep liquid, which is caused by the decrease in pressure as it is discharged from the reservoir, has resulted in the precipitation of metal-rich scales within the production wells[15]. These precipitates can be spectacularly enriched in gold, owing to very efficient deposition by boiling, as observed in many other geothermal systems[16–18].

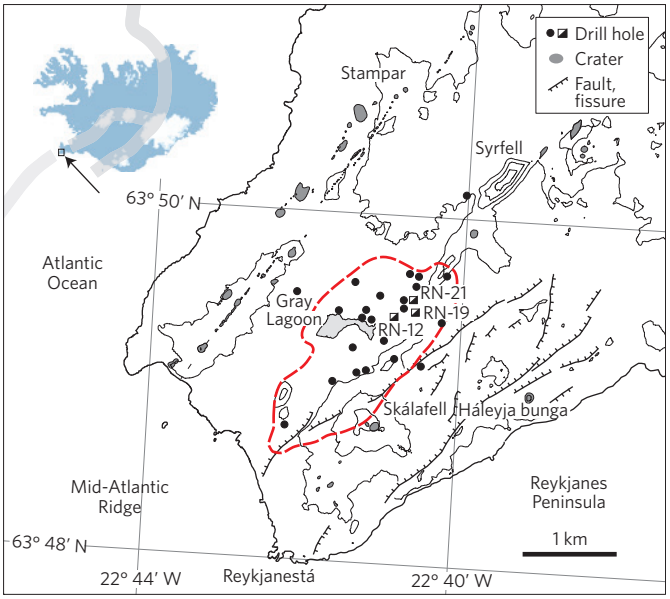

Figure 1 | Location of the Reykjanes geothermal system where the Mid-Atlantic Ridge emerges on Iceland. The map of the peninsula shows the locations of the sampled drill holes and the extent of surface alteration associated with the geothermal activity (red dashed line). The deep geothermal reservoir occupies an area 2.5 km in length × 1.5 km in width to a depth of at least 2 km (ref. 10).

Twenty-eight geothermal wells have been drilled in the Reykjanes field, and 16 have been brought into production. In May 2006, a 100 MW power plant was commissioned, and in 2007 an average of 736 kg s^{-1} of brine was produced from the wells[10,14]. This was decreased to 518 kg s^{-1} in 2013. The deepest wells have now been drilled to 3 km below sea level to continue tapping reservoir liquids that are in excess of 300 °C (ref. 14). One year after the commissioning of the power plant, we sampled the deep liquids in three wells (RN-12, 19, and 21) at depths several hundred metres below the bottom of the boiling zone, which was located at ~1,350 m when the wells were closed[8]. Since then, the depth of boiling in the same wells has descended to at least 1,500 m. In 2014, we re-entered the wells and collected reservoir liquids at depths of between 1,575 and 1,650 m in the first ever time-series experiment of this type. The samples were collected during a short period of maintenance at the power station while the wells were discharging at very low rates (3–5 kg s^{-1}) compared with the normal production flow rates.

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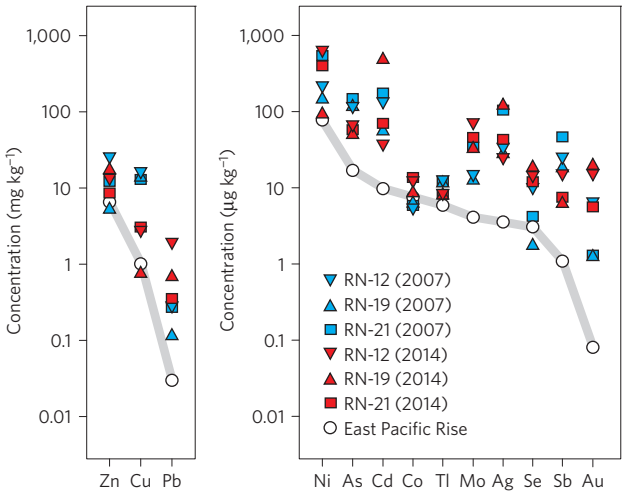

Figure 2 | Trace metal concentrations of the deep geothermal brines at Reykjanes compared with typical mid-ocean ridge black smoker fluids from the East Pacific Rise. Metal concentrations in the deep liquids are many times higher than in mid-ocean ridge black smoker fluids, especially Cu (up to ~10×), Pb (~30×), Ag (~20×), and Au (~100×), but show very similar metal ratios.

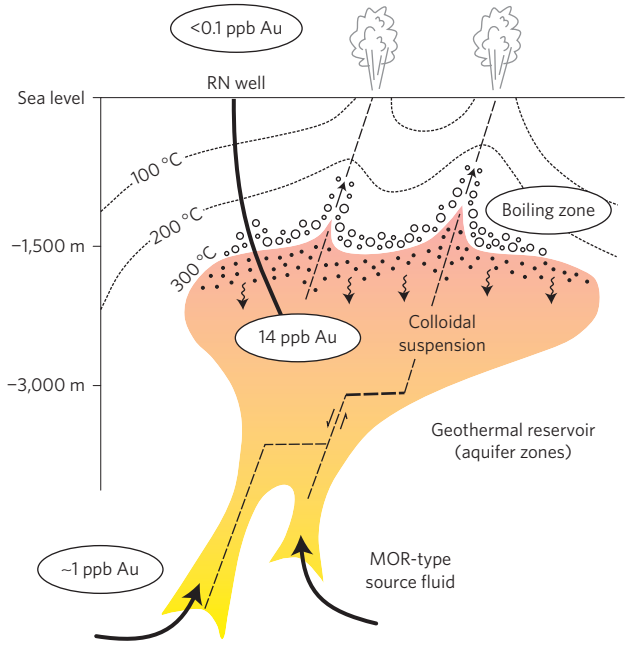

Figure 3 | Schematic representation of the deep geothermal reservoir showing conditions leading to the accumulation of gold in the deep liquids. The very high concentrations are interpreted to be a consequence of evolving reservoir dynamics whereby boiling causes the nucleation of gold colloid that becomes enriched below the boiling zone. MOR, mid-ocean ridge.

A custom-built titanium downhole sampler, previously deployed in active geothermal systems in New Zealand and Papua New Guinea, was used for the sampling[19]. All samples were taken above the main inflow near the bottoms of the wells and below the level of first boiling, indicated by downhole pressure and temperature measurements (see Supplementary Fig. 1).

Since the beginning of power production, the pressures in the reservoir have dropped by as much as 40 bars, but the concentrations of the major elements in all three wells have remained very similar (Table 1). Na, K, Ca, SiO_2 and Cl (~18,000 parts per million) are essentially the same in both the downhole samples and in discharging liquids at the surface (see Supplementary Table 1). Unlike samples collected at the surface, which are always clear liquids, all of the samples from the deep reservoir were notably discoloured owing to suspensions of fine particles. The particulate matter, which resembles 'smoke' in black smoker fluids, is interpreted to have precipitated inside the sampler during recovery, as a result of cooling and in response to vapour loss when the sampler was opened. When redissolved in the liquid, the smoke particles account for about 60% of the metal in the samples (Supplementary Table 1). The total metal concentrations in the deep liquids, especially Cu, Pb, Ag and Au, are many times higher than in mid-ocean ridge vents, but the proportions of the different metals in 2014 and in 2007 closely matched those of black smokers (Fig. 2).

The formation of sulfide mineral scales in the near-surface pipes and at the well heads confirms that the geothermal solutions are saturated with respect to metal sulfides at reservoir conditions[15]. In most of the wells, sulfide precipitation from rising hydrothermal fluids starts at the onset of boiling and continues to the surface. This raises the possibility that some of the metal in the deep liquids is from mineral scales inadvertently collected by the downhole sampler. However, because the samples were collected well below the boiling level in each hole, the presence of mineral scales at the sampling depth is unlikely. Moreover, the consistent enrichments of trace elements in all three wells, both in 2007 and 2014, argue strongly against random contamination by foreign particles. In 2007, the concentrations of gold in the reservoir liquids were between 1 and 6 ppb; in 2014, the concentrations in the same wells were between 5 and 21 ppb (Table 1). RN-12 had the highest concentration in 2007 and contained 16 ppb Au in 2014. According to experimental data[20,21], the ΣAu solubility in the Reykjanes deep liquids at *in situ* temperature and pH should be ~1 ppb Au (that is, the solubility of all aqueous sulfur complexes of Au; see Supplementary Information). Thus, the sampled liquids are about 10× oversaturated in gold. By comparison, the concentrations of gold in typical mid-ocean ridge black smoker fluids are only 0.06 to 0.2 ppb (Table 1). Although mid-ocean ridge systems equilibrate at higher temperatures (to 400 °C), owing to the higher pressures[22], they do not show higher concentrations of Au in the endmember fluids.

The increase in the gold concentrations of all of the wells since 2007 is most reasonably interpreted as a consequence of the drawdown of the geothermal liquid following installation of the power plant, which led to a sharp pressure drop and increased boiling in the reservoir zone[14]. An increase in pH and loss of H_2 from the reservoir liquids in response to boiling could have resulted in an increase in the solubility of gold[23,24], causing more gold to be leached from the adjacent formations. However, well monitoring shows that the pH and H_2 concentrations have not changed significantly over time, and the reservoir liquids have remained uniformly reducing[13,14]. Our findings indicate that gold is oversaturated at reservoir conditions, which we interpret to mean that a significant amount of gold in the reservoir must be present as dispersed particles (that is, nanoparticles or colloids) that were sampled with the liquid phase. Gold that was precipitated in one part of the upflow, most likely as a result of the increased boiling, must be entering the aquifer zones as a colloidal suspension, leading to the apparent oversaturation of the reservoir liquids[25,26]. Owing to the negative surface charge of the particles, which causes them to repel each other, gold colloids may remain in suspension indefinitely in saturated liquids. In the presence of high silica, the gold particles may also be dispersed among similarly charged colloidal silica, and this suspension can remain stable up to 350 °C (refs 25,27). These suspensions may be destabilized by changes in pH or by physical interaction with mineral surfaces of scales, and the deposition of colloids is strongly suggested by the

Table 1 | Major and trace metal analyses of downhole liquids from the Reykjanes geothermal wells in 2007 and 2014.

Drill hole		RN-12	RN-12	RN-19	RN-19	RN-21	RN-21	EPR	Sea water
Year		2007	2014	2007	2014	2007	2014	Vents	
Sample depth (m)		1,500	1,650	1,500	1,600	1,350	1,575	2,600	
Reservoir temp. (°C)		314	302	302	279	285	281	~350	2
pH (25 °C)		4.84	4.67	4.80	4.72	4.89	4.81	3.4–3.8	7.8
Major elements									
Na	mg kg^{-1}	9,035	8,253	8,943	8,835	9,127	8,494	9,932	10,667
K	mg kg^{-1}	1,486	1,186	1,486	1,281	1,603	1,238	907	395
Ca	mg kg^{-1}	1,884	1,544	1,683	1,375	1,763	1,422	625	409
Mg	mg kg^{-1}	9.5	12.2	1.9	7.2	4.1	8.4	0	1,269
Fe	mg kg^{-1}	24.0	63.4	8.60	59.6	136	85.1	92.9	2.8×10^{-5}
Si	mg kg^{-1}	281	356	318	295	318	301	494	1.97
Cl	mg kg^{-1}	18,580	18,520	18,120	17,570	18,720	18,750	17,340	19,150
SO_4	mg kg^{-1}	16.1	15.0	19.5	18.4	16.2	17.5	0	2,712
CO_2	mg kg^{-1}	1,648	2,374	1,091	873	722	678	930	na
H_2S	mg kg^{-1}	48.5	66.8	32.8	24.2	24.9	26.0	250	0
H_2	mg kg^{-1}	0.20	0.12	0.43	0.41	0.23	0.36	0.86	6×10^{-7}
Trace metals									
Zn	mg kg^{-1}	25.7	13.3	5.2	16.7	12.4	8.8	6.9	0.0003
Cu	mg kg^{-1}	16.6	2.9	13.2	0.8	13.2	3.1	2.2	0.0002
Pb	μg kg^{-1}	269	1,991	124	698	290	362	63.8	0.0021
Ni	μg kg^{-1}	235	654	117	94	528	392	81	0.47
As	μg kg^{-1}	113	67	113	51	150	58	19	1.7
Cd	μg kg^{-1}	135	38	56	491	180	71	9	0.067
Co	μg kg^{-1}	<10	12.2	<10	8.8	<10	14.2	7.8	0.0012
Tl	μg kg^{-1}	11.0	8.3	11.0	8.2	12.1	8.3	6.5	0.014
Mo	μg kg^{-1}	15	73	12	33	32	46	4	10
Ag	μg kg^{-1}	35	26	27	121	104	44	4	0.0022
Se	μg kg^{-1}	10.0	15.1	1.7	18.0	4.2	12.1	5.7	0.13
Sb	μg kg^{-1}	25	16	18	6.3	46	7.7	1.1	0.195
Au	μg kg^{-1}	6.1	16.2	1.2	20.9	1.4	5.7	0.08	3×10^{-5}

Reservoir temperatures were calculated from the quartz geothermometer (ref. 14). Concentrations in milligram per kilogram and microgram per kilogram of solute water have been adjusted for vapour loss and total dissolved salts. pH and gas concentrations are calculated from surface samples collected between 2007 and 2014 (ÍSOR Reports 2013/015 to 2015/010); gas concentrations are uncorrected for recent excess enthalpy conditions (see Supplementary Information). Data for East Pacific Rise (EPR) vent fluids are from the OBS vent site at 21° N, except for Ni, Mo, Sb and H_2, which are from Juan de Fuca Ridge vents (N. Cleft and Endeavour), and Co, Cd, Tl and CO_2, which are average values for EPR vents. pH for EPR vent fluids is the measured pH at 25 °C. The reported Au concentration for seafloor vents is the average of six published values from different sites described in ref. 9; see Supplementary Information for additional details and references.

well-developed colloform textures of gold-rich scales in the upper parts of the wells[15].

The reservoir at Reykjanes contains about 7.5×10^8 m^3 of geothermal brine[10]. With a current load of ~14 μg kg^{-1} Au (average of the 3 sampled wells in 2014), the reservoir holds ~10,000 kg of gold. Gold-rich scales are forming in the boiling zone, and gold may also be deposited in deeper aquifer zones, but the concentrations in the surface brines are close to the detection limit in all cases (Supplementary Table 1), indicating that virtually no gold is making it to the surface. Therefore, gold must be accumulating in the reservoir and in the boiling zones at about the same rate that it is being introduced into the system (Fig. 3). A source liquid containing ~0.1 ppb Au, similar to mid-ocean ridge black smoker fluids, could account for most of the gold in the reservoir if it has been accumulating in this way since the last glacial maximum[13]; a saturated liquid containing ~1 ppb Au could have provided all of the gold in just 3,000 years. Episodic outflow that matches the natural inflow (at ~100 kg s^{-1}), but now with a gold concentration of 14 ppb, could completely evacuate the gold from the reservoir in less than 300 years. A dynamically self-adjusting system that slowly accumulates gold and then periodically flushes it into the surrounding rocks could produce a sizable gold deposit.

The concentration of gold in the reservoir at Reykjanes is at least as high as that found in the source fluids of some actively forming gold deposits in island arcs[3,4], so it is unclear why there are no major gold deposits associated with the Reykjanes geothermal system. Large, high-grade gold deposits are formed only when metal-rich fluids released from a hydrothermal reservoir are focused into favourable depositional settings—a relatively rare occurrence resulting from the complex interplay of varying crustal permeability and fluid flow[3,28]. In the absence of a focusing mechanism, metal accumulated in the deep geothermal reservoir at Reykjanes is most probably lost to the subsurface fracture network, and no significant concentrations of ore are formed, as observed in other large-scale geothermal systems[2,3]. Gold that is not released to the surface is dispersed within a volume at least as large as the reservoir itself and thus would be preserved only as a minor geochemical anomaly in the rock record (for example, 10,000 kg Au added to 7.5×10^9 m^3 of basalt with 10% effective porosity would increase the gold content of the rocks in the reservoir volume by only ~0.5 ppb Au). Scenarios involving continuous mass transport through the reservoir, as in mid-ocean ridge hydrothermal systems[22], also cannot reproduce the gold concentrations observed in our study. Some authors have suggested that the Iceland plume itself may be an enriched source of gold or that metals may be degassed directly from mafic melts[29,30]. Instead, we suggest that the non-conservative behaviour of metals in the geothermal system at Reykjanes explains how the reservoir liquids have become so enriched in gold and, if released into a small volume of rock, could contribute to the formation of high-grade gold mineralization.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

All authors participated in the fieldwork, the design of the study, and the analysis of the data. M.H. and V.H. prepared the manuscript with D.G.-S. and K.L.B. The sampling programme was managed by V.H., together with ÍSOR and HS Orka staff. K.L.B. provided the downhole sampler and oversaw the deployments. D.G.-S. conducted the laboratory analyses. All authors discussed the results and contributed to the writing of the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.H.

Competing financial interests

The authors declare no competing financial interests.

Methods

The titanium downhole sampler used in this study was purpose-built by GEOKEM to recover reservoir liquids for trace metal analysis. The sampler is the only one of its kind in the world and has been used to recover similar samples from a number of different geothermal systems[3–5,8]. The procedures for deploying the instrument were identical to those in previous studies. The sampler is lowered from the surface on a wireline through a hydraulic seal at the wellhead to the desired depth and then opened by an inertial trigger. The trigger pierces a stainless-steel shim and permits fluid to enter the sampler under pressure through a narrow hole (1–3 mm diameter); up to 830 ml of liquid may be recovered. A titanium non-return valve with a Viton seal prevents fluid from escaping the vessel, although very high vapour pressures may overcome the spring mechanism with some loss of steam. Procedural blanks subjected to the same thermal effects of downhole sampling and using the same sampler confirm that there is little or no contamination when samples are being collected (see Supplementary Information).

All of the wells were 'shut in' for 24 h before sampling during a brief period of maintenance at the power station. RN-12 was sampled on two consecutive days, and reservoir liquids were successfully recovered at 1,650 m depth (150 m below the two-phase flow). RN-19 was sampled only once from 1,600 m depth (50 m below the two-phase flow). RN-21 was sampled twice, 2 days apart, and reservoir liquids were recovered from 1,575 m depth. Details of the sample collection in each well are provided in the Supplementary Information. At the surface the sampler was cooled and then opened to retrieve the solution. Samples were collected in pre-washed high-purity PFA (perfluoralkoxy) plastic bottles, which were subsampled in the field into smaller PFA bottles. All samples were discoloured by a suspension of fine particles, assumed to have precipitated from solution when the sampler was brought to the surface, cooled and the gases expelled. After thoroughly resuspending any particles by shaking, a split was taken to filter and analyse separately, and the original unfiltered sample was acidified with subboiled HNO_3 to return the suspended material to solution. The titanium vessel was then rinsed with aqua regia to dissolve any metals that may have adhered to the internal walls, and the cleaning acid was collected and analysed. In this way, all metals that may have precipitated in the sampler during its return to the surface were incorporated into the final volume. All samples were analysed in the ICPMS Laboratory of the Institute of Geosciences, Kiel University. Major elements were determined by inductively coupled plasma optical emission spectrometry, and trace elements by inductively coupled plasma mass spectrometry. Details of the procedures, analytical uncertainties, repeat analyses, and blanks are provided in Supplementary Tables 2 and 3. The results for the different subsamples were combined to obtain the reported concentrations for the reservoir liquids in Table 1. All measurements were corrected for steam loss and recalculated to milligrams per kilogram and micrograms per kilogram of solvent water.