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MINERAL DEPOSITS RECOVERED FROM NORTHERN GORDA RIDGE: MINERALOGY AND CHEMISTRY

by

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NOTICE

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ABSTRACT

The Gorda Ridge is the only submarine volcanic ridge within the newly proclaimed Exclusive Economic Zone of the United States. In 1988 a team of divers discovered hot springs on the northern segment of Gorda Ridge and recovered rock and mineral samples from this hydrothermal field. Here we report the mineral and chemical composition of these samples.

INTRODUCTION

Gorda Ridge

Gorda Ridge is a relatively short (300 km) segment of volcanic, ocean ridge that extends from the Mendocino Fracture Zone (40° 20' N) to the Blanco Fracture Zone (43° 00' N) off the coast of Oregon and California (Figure 1). The whole length of the ridge is within 200 nautical miles of the United States. The shape and average depth of the ridge is similar to slowly spreading ridges in other oceans, such as the Mid-Atlantic Ridge. The Gorda Ridge axial valley is more than 3,000 m deep and some depressions are as deep as 3,800 m (Clague and Holmes, 1987).

As seen in Figure 1, the Gorda Ridge is divided into three segments by two short offsets, and the northern segment extends from 42° 26' to 43° 00' N. This northern segment of Gorda Ridge has been the center of extensive study for the past nine years. Cruises there in 1980, 1981, 1983, 1985, and 1986 mapped the ocean floor with SEABEAM and SeaMARC II sidescan sonar, dredged basalts from the axial valley of Gorda Ridge and from the Blanco Fracture Zone, collected sediment cores and water samples, and measured water temperature. One dive with the submersible ALVIN was made to the sea-floor (Malahoff, 1985). These studies led to five dives with the submersible SEA CLIFF in 1988, and the discovery of a new hydrothermal vent field (Rona et al., 1988).

The northern Gorda Ridge appears to be a single rift volcano that has its highest elevation (3,000 m water depth) at $42^{\circ} 47' \text{ N}$ (Figure 2). At this location the rift valley is narrowest (about 7 km) and axial valley walls are only about 500 m high (Clague and Holmes, 1987). Both to the north and south, from $42^{\circ} 47' \text{ N}$, the valley gets wider and deeper and the walls of the axial valley are higher. At the intersection of the ridge and the Blanco Fracture Zone the axial valley is more than 15 km wide and has a depth of 3,500 m. South of the saddle the axial valley descends to its greatest depth of 3,800 m (Clague and Holmes, 1987) which suggests that the magma supply is low in this area.



Features of the northeastern Pacific Ocean basin near Gorda Ridge. The rates of motion in mm/yr are given for the Pacific Plate and the Juan de Fuca Plate south of the Blanco Fracture Zone. The northern section of the Gorda Ridge (labeled N) is shown in detail in Figure 2. The approximate location of the Cascadia subduction zone is indicated by the solid line with triangles. Cascade volcanos are indicate by isolated triangles. Figure from Fisk and Howard (1989).



Topographic features of the northern segment of Gorda Ridge. Sites that were suspected to have hydrothermal activity based on studies in 1985 are indicated by squares and labeled GR-14 and GR-15 after Collier et al. (1986). Locations of dredged rocks are indicated by circles. The locations of two dives by Malahoff (1985) are indicated by triangles and labeled A1406 and A1407. GR-14 was the site of SEA CLIFF dives 767 to 771 that collected the samples discussed in this report. Contour interval is in meters. Figure from Fisk and Howard (1989). Basalts were initially collected from this segment of the ridge in 1968 and 1976 by Oregon State University and their chemistry and mineralogy were reported by Kay et al. (1970) and Wakeham (1978). The first indication of hydro-thermal activity on the northern Gorda was the presence of slightly elevated temperatures, high manganese concentrations, and increased particle concentrations in the water within 400 m of the sea-floor at 42° 44.7' N, 126° 43.7' W and at 42° 57.1' N, 126° 35.0' W (Collier et al., 1986, Baker et al., 1987). These were designated Site GR-14 and Site GR-15, respectively, (Figure 2) and both sites continued to exhibit these anomalous signals later the same year (Collier and Baker, 1989).

Another indication of hydrothermal activity on the northern Gorda was the presence of barite and pyrite on basalts dredged from 3,775 m at the south end of this segment (Clague et al, 1984). Both of these minerals are associated with hydrothermal activity on other oceanic ridges. In 1985 photographs of the axial valley near hydrothermal site GR-14 showed that some rocks appeared to be covered with bacterial mats that often grow near areas of hydrothermal activity (Clague and Rona, 1989). Changes in sediment color and texture were also observed in the photographs which suggested the presence of hydrothermal precipitates. One sediment core from the area also contained high copper content, another indication of hydrothermal action (Nelson 1987, personal communication).

Thin, black to brightly colored layers of minerals were removed from rocks collected from the axial valley near Site GR-14 in 1985 (Clague and Holmes, 1987) and from rocks that had previously been collected from this area (Howard, 1989). These layers proved to contain minerals and chemical indicators that suggested the presence of hydrothermal activity in two areas near GR-14. This area was again dredged in 1986 and basalts were recovered with a 1 to 3 mm-thick coating of boehmite.

Boehmite had previously been reported on the Middle Gorda (Clague et al., 1984; Clague and Holmes, 1987) but it was not known whether it was a hydrothermal precipitate or a weathering product of the basalt. Close examination of the sample indicated that the boehmite was a product of weathering of the basalt by reaction with silica-poor water that was 200° to 300°C (Howard and Fisk, 1988).

Dive locations

Five dives were made in the vicinity of Site GR-14 (Figure 2). Three of these (767, 768, and 769) were on a long hill with its axis parallel to the ridge and two dives were in the deepest part of the valley near Alvin dive 1407. The tracks of dives 767 and 768 are shown in Figure 3 and dive



Schematic diagram of the eastern side of the axial valley at GR-14. The long hill is indicated with the light stipple. The approximate path and end points (x) of SEA CLIFF dives 767 and 768 are shown. The hydrothermal field from which samples from dives 767, 768, and 769 were collected is shown with the dense stipple. Contour interval is in meters.

769 traversed the southern end of the hydrothermal field. The first dive traversed eastward from east side of the axial valley until reaching the long hill and then turned south and maintained a depth of about 2750 m. Evidence of hydrothermal activity was first observed along the side of the hill. A sample of hydrothermal crust was collected (sample 767-3) and the dive was terminated at a site of active chimneys (Figure 4). Dives 786 and 769 returned to the hydrothermal field and determined its extent to the north, south, and east and collected additional samples including another hydrothermal crust (769-1) and pieces of an active chimney (769-3 and 769-4). Dive 768 observed some inactive chimneys (Figure 4) but no samples of these chimneys were recovered.

Two dives (770-771) were made in the deepest part of the axial valley near GR-14 and although no hot springs were discovered, samples of rocks that had been altered by hot water were recovered (sample 771-2).

One of the most peculiar features of the hydrothermal field was the presence of a crust that covered an area of about 10,000 m^2 near the active chimneys (Figure 4). The crust lay on sediment that appeared to be devoid of life and had shimmering water rising from it. The sediment itself was hot; a temperature probe reached 100°C when inserted into the sediment for a few seconds.

Samples

Samples were collected on dives 767, 768, 769, and 771 and brief descriptions of the samples are given in Table 1. These samples include the crust that formed over sediment in the hydrothermal field, pieces of active hydrothermal chimneys and basalt. Core samples were taken on dives 767 and 768 and these were distributed to Terry Nelson at NOAA in Miami and are not part of this report. The hydrothermal crusts (samples 767-3 and 769-1) were about 10 cm thick and were soft and friable. These crusts overlay sediment that appeared to be warm, and close to where sample 767-3 was collected, the sediment temperature was as much as 100°C. No macroscopic animals were observed on the crust in situ but sponge spicules and tube worm "burrows" were found in the hand specimen. Crust 769-1 was friable and broke into several pieces while being examined on board. It was brightly colored and appeared to be made of several varieties of minerals. Subsamples of the crusts were analyzed by X-ray diffraction for mineral identification and by atomic absorption for chemical identification.

Several samples of undifferentiated sediment and debris from the hydrothermal field were collected on dive 768 appeared to be mostly iron



Contour map of the southern end of the hill shown in Figure 3. The features identified during dives 767 to 769 are indicated in the legend. Approximate locations of selected samples from Table 1 are indicated. Diagram from Rona et al. (1989). Note: north is to the left.

| Sample | Weight | Description | Mineralogy |
|--------|--------|---|--|
| 767-3 | 200 g | hydrothermal crust overlying high temperature soft sediment in SEA CLIFF vent field | hydrothermal clay Fe oxyhydroxide Mn oxide amorphous silica atacamite(?) |
| 768-1a | 5 g | rubble from inactive portion of SEA CLIFF vent field | hydrothermal clay amorphous silica Fe oxyhydroxide |
| 768-1b | 50 g | hydrothermal debris from inactive portion of SEA CLIFF vent field | hydrothermal clay (nontronite ?) Fe oxyhydroxide talc (?) |
| 768-1c | 50 g | hydrothermal debris from inactive portion of SEA CLIFF vent field | hydrothermal clay (nontronite ?) amorphous silica talc ? Fe oxyhydroxides |
| 768-3 | 50 g | hydrothermally altered basalt frag- ment from the active part of the SEA CLIFF vent field | hydrothermal clay (nontronite ?) talc ? pyrite |
| 769-1* | 3500 g | hydrothermal crust from vent field | hydrothermal clays Fe oxyhydroxide Mn oxides pyrite calcite amorphous silica anyhdrite/barite |
| 769-2 | 4500 g | basalt pillow fragment with hydro- thermal precipitate | basalt: plagioclase glass precipitates: Mn oxide Fe oxyhydroxide hydrothermal clay (nontronite ?) |

 Table 1. GR-14 1988 SEA CLIFF Sample Description and Preliminary Shipboard Mineral Identification

Table 1 (continued)

| Sample | Weight | Description | Mineralogy |
|--------|---------|--|--|
| 769-3 | 50 g | chimney fragments active from grey smoker spire | anhydrite amorphous silica pyrite wurtzite/sphalerite barite(?) goethite lepidocrosite Mn oxide (?) calcite realgar(?) sediment and basalt clasts |
| 769-4 | 50 g | chimney samples from active grey smoker spire (same location as 769-3) | same as for 769-3 |
| 771-1 | 50 g | basalt sheet flow | basalt glass plagioclase olivine |
| 771-2 | 200 g | basalt pillow fragment with hydro- thermal alteration | basalt glass plagioclase olivine Mn oxide boehmite Fe oxyhydroxide smectite/chlorite |
| 771-3 | 3,500 g | basalt pillow fragment | basalt glass plagioclase olivine augite (?) Fe oxyhydroxide Mn oxide |

* Some pieces were frozen to preserve biological material (bacterial mats, limpets and tubeworms).

oxyhydroxides and amorphous silica. One basalt fragment in the debris was altered to hydrothermal clay on the exterior. Basalts from dive 771 in the axial valley also were altered but, except for sample 771-2, the alteration was not extensive. Sample 771-2 had a coat of boehmite that suggests alteration at 200 to 300°C.

Fragments of an active chimney were recovered on dive 769, these samples were fragile and appear to be poorly cemented with amorphous silica. Subsamples of the chimney sample was analyzed by X-ray diffraction and by atomic absorption.

METHODS

X-Ray Diffraction

X-ray diffractograms were obtained using an automated SCINTAG X-ray diffractometer. The sample was mounted on a glass disk and rotated while the detector scanned continuously at 1 degree per minute over the 2 θ range of 2° to 70°C. Identification of clay minerals required glycolation to determine expansions of 001 basal reflections. Background signals were removed from the spectra and peaks were selected by a computer routine. The peaks of commonly occurring minerals in hydrothermal deposits accounted for most of the peaks in the diffractograms.

Atomic Absorption

Atomic absorption analyses were completed using standard techniques on a Perkin-Elmer 5000 atomic absorption spectrophotometer. The samples were analyzed for aluminum, barium, calcium, copper, iron, lead, magnesium, manganese, nickel, potassium, silicon, sodium, and zinc. The precision for most elements was within $\pm 2\%$ and was within 4% for barium, iron, and silicon. Chemical analyses of standard rocks are shown in Table 2 and show that the agreement for most elements with the accepted literature values is acceptable.

RESULTS

X-ray diffractograms for the hydrothermal crusts (samples 767-3 and 769-1) are shown in Figures 5, and 6. Figure 5 is for subsample 3 from the top surface of crust 767-3 and this shows that the crystalline material of the upper surface is primarily barite. The diffractogram for the top surface of crust 769-1 also indicates barite is the main crystalline phase. The diffractogram for the interior of sample 769-1 (subsample 3b, Figure 6) shows that there is a zone of chaclopyrite and sphalerite within the crust. A similar zone was not sampled in crust 676-3 but pyrite peaks

| SAMPLE | <u>Al</u> (%) | <u>SiO</u> 2 (%) | <u>Fe</u> (%) | <u>Ca</u> (%) | <u>Mg</u> (%) | <u>Na</u> (%) | <u>К</u> (%) | <u>Mn</u> (µg/g) | <u>Ва</u> (µg/g) | <u>Си</u> (µg/g) | <u>Zn</u> (μg/g) | <u>Ni</u> (µg/g) | <u>Рb</u> (µg/g) |
|------------|------------------|---------------------|------------------|------------------|------------------|------------------|-----------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 767 3-3 | 0.74 | 56.36 | 0.63 | 0.08 | 2.37 | 0.45 | 0.13 | 85 | 48900 | 379 | 21730 | 30 | 84 |
| 767 3-5 | 0.29 | 67.70 | 8.27 | 0.19 | 1.91 | 0.78 | 0.11 | 79 | 21600 | 19900 | 1520 | 80 | 1230 |
| 768 1A | 1.58 | 58.84 | 1.40 | 0.10 | 18.25 | 0.70 | 0.07 | 336 | 0 | 198 | 370 | 0 | 0 |
| 769 1-1 | 1.04 | 69.13 | 0.90 | 0.09 | 1.72 | 0.54 | 0.21 | 83 | 49500 | 326 | 383 | 0 | 214 |
| 769 1-2 | 0.46 | 85.89 | 1.65 | 0.03 | 0.64 | 0.13 | 0.06 | 59 | 26700 | 717 | 2740 | 0 | 387 |
| 769 1-3A&B | 0.07 | 15.12 | 21.99 | 0.03 | 0.75 | 0.14 | 0.03 | 151 | 2490 | 207200 | 67300 | 30 | 562 |
| 769 3-1 | 0.83 | 81.53 | 1.10 | 0.08 | 0.53 | 0.45 | 0.11 | 51 | 30700 | 373 | 427 | 0 | 366 |
| 769 3-2 | 0.10 | 4.63 | 0.16 | 27.27 | 1.56 | 0.18 | 0.01 | 79 | 444 | 647 | 2000 | 0 | 70 |
| 769 4-1 | 1.16 | 40.38 | 6.24 | 5.34 | 6.43 | 1.04 | 0.14 | 403 | 8330 | 7660 | 4740 | 0 | 634 |
| 769 4-1dup | 1.12 | 40.60 | 4.40 | 5.33 | 6.40 | 1.05 | 0.14 | 394 | 10800 | 7490 | 4710 | 0 | 617 |
| 769 4-2 | 0.66 | 77.76 | 2.03 | 0.29 | 0.06 | 0.60 | 0.10 | 934 | 43000 | 640 | 310 | 0 | 343 |
| 771-2 | 34.41 | 11.31 | 3.40 | 0.10 | 0.06 | 0.50 | 0.27 | 4012 | 129 | 80 | 80 | 240 | 45 |

Table 3. Atomic Absorption Analyses of Hydrothermal Material from Gorda Ridge



Diffractogram showing the presence of barite in sample 767-3 (subsample 3) from the top of the hydro-thermal crust. The vertical scale on the right is the relative peak intensities in percent, 2 θ angle is on the horizontal scale. The vertical scale on the left is the peak intensity in counts per second. The major peaks for barite (B) are present as well as several unidentified minor peaks.



Diffractogram for sample 769-1 (subsample 3b) which is a sulfide-rich zone within the hydrothermal crust. The material appears to be primarily chaclopyrite (Cp) and sphalerite (Sp). This is in agreement with the high iron, copper and zinc found in this sample.

were observed in one diffractogram for this sample. The base of the crusts did not produce strong diffraction peaks.

Atomic absorption analyses (Table 3) show that silica makes up a large part of the hydrothermal crusts. This must be amorphous silica because no quartz or silica rich minerals were found in the X-ray diffraction study. These crusts also have a significant amount of barium as would be expected from the X-ray diffraction pattern. Parts of both crusts (767-3 and 769-1 have high copper concentrations and one also has about 7 wt % zinc. These elements correspond to the chalcopyrite and sphalerite mineral identifications in sample 769-1-3 (Figure 6).

X-ray diffractograms for the fragments of chimney that were recovered on dive 769 show that they are primarily anhydrite and barite (Figures 7 and 8). The primary mineral phase of the interior dense part of the chimney (769-3-1) is barite (Figure 7), but the atomic absorption analyses shows that barium makes up about 3 wt % of the chimney so the mineral barite only contributes 5% to the weight of the sample, and the main chemical constituent is silica. The exterior of the chimney (769-3-2, Figure 8) is primarily anhydrite and the remainder is amorphous silica and clay. If all of the calcium in sample 769-3-2 (Table 3) is contained in the anhydrite, then 93 wt % of the sample is anhydrite. The manganese, copper, nickel, lead and zinc concentrations of the chimneys are all relatively low with copper reaching a maximum concentration of 0.8 wt % in a mixture of chimney debris from the SEA CLIFF sample basket.

A diffractogram for sample 771-2 (Figure 9) confirms the dominant mineral is boehmite but indicates that anatase, a titanium mineral is also present. Some elements may be present in relatively high concentrations but were not measured by atomic absorption. Certainly sulfur is present in the sulfide and sulfate minerals that were identified by X-ray diffraction. Minerals that make up less than 5% of the sample weight may not have been observed in the X-ray study. The mineral arsenopyrite may be present and the elements silver, antimony, selenium, cadmium, and bismuth could be present if comparison with similar deposits on the Escanaba Trough is appropriate (Koski et al., 1988).

DISCUSSION

The shipboard descriptions of samples collected with SEA CLIFF agrees with the laboratory analysis of the samples by X-ray diffraction and atomic absorption except that the manganese content of most samples is too low to support the observation of manganese-oxides on the surfaces of

| Table 2. | Atomi | ic Abso | rption 4 | Analyses | of Sta | indards | | | | | | | |
|-----------|-------|-------------|-----------|----------|--------|---------|------|-----------|-----------|-----------|-----------|--------|--------|
| SAMPLE | AI | <u>SiO2</u> | <u>Fe</u> | Ca | Mg | Na | к | <u>Mn</u> | <u>Ba</u> | <u>Cu</u> | <u>Zn</u> | Ni | Pb |
| | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (µg/g) | (µg/g) | (µg/g) | (µg/g) | (µg/g) | (µg/g) |
| BCR-1 | 7.02 | 55.82 | 9.33 | 5.06 | 2.08 | 2.44 | 1.42 | 1408 | 809 | 13 | 140 | 29 | 0 |
| BCR-1 (p) | 7.21 | 54.35 | 9.41 | 4.97 | 2.08 | 2.43 | 1.40 | 1409 | 678 | 18 | 129 | 13 | 14 |
| AGV-1 | 9.35 | 61.72 | 4.70 | 3.62 | 0.94 | 3.11 | 2.48 | 738 | 1404 | 62 | 94 | 24 | 15 |
| AGV-1 (p) | 9.07 | 59.25 | 4.73 | 3.53 | 0.92 | 3.15 | 2.41 | 740 | 1220 | 60 | 88 | 17 | 36 |
| MRG-1 | 4.38 | 39.36 | 12.34 | 10.51 | 8.07 | 0.53 | 0.15 | 1319 | 114 | 136 | 186 | 195 | 0 |
| MRG-1 (p) | 4.50 | 39.32 | 12.46 | 10.56 | 8.14 | 0.53 | 0.15 | 1316 | 50 | 135 | 240 | 195 | 10 |
| BLANK | 0.00 | 0.14 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 2 | 120 | -2 | -1 | 0 | 18 |

(p) is published and accepted value.



Figure 7

Diffractogram for sample 769-3-1, the interior of an active chimney from the Sea Cliff hydrothermal vent field. *B* indicates peaks for barite which appears to be the primary mineral phase. Minor pyrite (P) may also be present.



Diffractogram for sample 769-3-2, the exterior of the same active chimney from which sample 769-3-1 came. A indicates the X-ray peaks for anhydrite which appears to make up the majority of the sample. Peaks also indicate a small amount of clay is present.



Figure 9

Diffractogram for the exterior of sample 771-2. The major peaks for boehmite (Bo) are present as well as several peaks for the titanium-rich mineral anatase (At).

the hydrothermal crusts. The crusts in the Sea Cliff hydrothermal field are different from those found in the Galapagos hydrothermal area. In the Galapagos the crusts are primarily <u>well-crystallized</u> manganese oxides or well-crystallized, iron-rich clay (nontronite) with minor amounts of barite, quartz, plagioclase, calcite, and other clays (Corliss et al., 1978). In the Sea Cliff Hydrothermal Field, the crusts are primarily amorphous with barite, clays, and little or no manganese oxides. Sulfides (chalcopyrite and sphalerite) are present in Gorda Ridge crust, but are not found in the Galapagos mounds. In the Galapagos, the mounds have an active biologic community (Williams et al., 1979), but in the Sea Cliff Hydrothermal Field no animals colonized the crusts, presumably because they are too hot (sediments immediately beneath the crusts had temperatures of about 100°C) or because there was little flow through the crusts.

The basalt fragment (768-3) from debris collected from the sediment suggests that this sediment is at temperatures greater than 200°C. The exterior of this basalt was altered to mixed-layer clay and this reaction normally occurs at temperatures of 230 to 240°C (Kristmannsdøttir, 1983; Schiffman et al, 1988).

The chimney sample (769-3) has a dense interior and a porous exterior. The exterior is primarily anhydrite and is similar to the exteriors of chimneys from the East Pacific Rise (Hekinian et al., 1983), however the interior of this chimney is primarily barite, unlike those from the of the East Pacific Rise. Barite has been found in chimneys from sediment covered hydrothermal systems such as Guaymas and Escanaba (Koski et al., 1985; and Zierenberg et al., 1986) but barite is not commonly found in chimneys of sediment-free ocean ridges. The cause for this difference between chimneys from the northern Gorda and the Juan de Fuca, both sediment-free ridges, is not known.

SUMMARY

The presence of hydrothermal vents near site GR-14 was confirmed in dives with the submersible SEA CLIFF in 1988. The hydrothermal crusts (samples 767-3 and 769-1) are made of clays, barite, sulfides, and amorphous silica. Both crusts have barite occurring throughout but they also have mineralogic layering. At the base of the crust, amorphous silica, clay, and possibly albite are found. In the middle is a thin layer of chalcopyrite and sphalerite and at the top the primary crystalline mineral is barite. Both crusts contain clasts of clay (illite or mica), barite, and amorphous material. The chimney fragments (samples 769-3) are primarily sulfates and sulfides. The dense interior of the chimney is barite with minor pyrite while the more porous exterior is anhydrite.

Debris (samples 768-1,3) collected from the sediment of the hydrothermal field includes a basalt fragment that is weathered to a mixed layer clay (smectite and chlorite), and a 3 mm thick fragment of crust that is reddishbrown to light-yellow and consists of clay and possibly pyrite.

A 2 to 4 mm thick, white crust on a basalt fragment from the axial valley (sample 771-2) was primarily boehmite with minor anatase. Although no hydrothermal activity was observed in the axial valley where this sample was collected, the presence of boehmite suggests that hydrothermal water with temperatures over 200°C (Howard and Fisk, 1988) had occurred at The highest water temperature measured in the hydrothermal this site. field was 270°C. Samples were collected from the chimneys as well as from the sediments that surrounded the chimneys. The samples are unusual in their chemistry because of the high barium content. The samples of hydrothermal crust are composed primarily of amorphous silica as well as minor amounts of sulfates, oxides, sulfides, and clay. The whole hydrothermal field was not surveyed, but an estimate of the total copper content of the surveyed portion of the field is 20 tons. In addition, there is about 40 tons of barium. The presence of a second hydrothermal system near GR-14 is suspected as well as one near GR-15, but these hydrothermal fields have not yet been confirmed.

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