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MECHANISM FOR MERCURY DEPOSITION AT NGAWHA SPRINGS, NEW ZEALAND

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(with one text figure)

ABSTRACT

Elemental mercury is the source of mercury for current cinnabar deposition at Ngawha Springs, New Zealand. The deposition of cinnabar is strictly weather dependent for most of the area, occurring only during and just after rain. During these periods pH and Eh drop favouring oxidation of mercury at suitable sites; such conditions prove to be necessary and sufficient from laboratory experiments.

MERCURY DEPOSITION

Ngawha Springs, 250 km north of Auckland, is a site of present day cinnabar deposition (Davey and van Moort, 1974). This and other nearby deposits are associated with Tertiary and Quaternary hydrothermal activity. Small scale mining has taken place at Ngawha, but now balneal establishments have been erected adjacent to the ore deposits and fumaroles.

The springs are situated in a drained, insilted lake basin, below which is a chaos of marine sediments hundreds of metres thick (Fleming, 1945 and N.Z.G.S. Rept. 16, 1966). The area is surrounded by many Pliocene to Holocene basalt flows. It is probable that the present activity is associated with a shallow basaltic intrusion. The springs are up to 65^{o}C, and do not discharge 'thermal' water. Heat is supplied by the ascending hot gases; composed of CO_2, CH_4, H_2O, NH_3, H_2S and Hg. The 'gas' to steam ratio is about 1,000 times that of Wairaki; thus it is dry by world standards.

Cinnabar is found in the hotter areas and coats various materials. It also occurs in stream sediments with sulphur, but is nowhere massive. During and after appreciable rain, but not at other times, cinnabar is conspicuously abundant in water courses, which also contain colloidal and freshly precipitated sulphur. The exposure of pyritic materials from the hot ebullient baths causes cinnabar coatings to appear in a couple of days.

During rainy periods Eh and pH generally drop markedly in most local waters, particularly where sulphurous gases percolate. In a period of drizzle, a pH less than 1.5 was recorded in the Ngawha Stream, normally with a pH of 4. Sufficiently high Eh's are present to cause formation of haematite and pyrolusite; i.e. Eh is more negative than -·9V for a pH of about 2 (Garrels and Christ, 1965).

The only detectable mercury species found coming into the area was elemental mercury. The major quantity is transported by gases at 35^{o}C or more (fig. 1). The mercury concentration was saturation level in all gases found in the central active area. Most confined water associated with the gases were also saturated with mercury metal.

From the above observations and others, the deposition of mercury proceeds via oxidation in acid waters during rain, which supplies oxygen. There follows a fast reaction with dissolved sulphide present to yield metacinnabar (black) and cinnabar (red), to which the former soon changes. Laboratory simulation of the field conditions showed that the presence of air or oxygen was essential to the formation of cinnabar. Without air present no cinnabar could be formed even after several months, contrasting with the

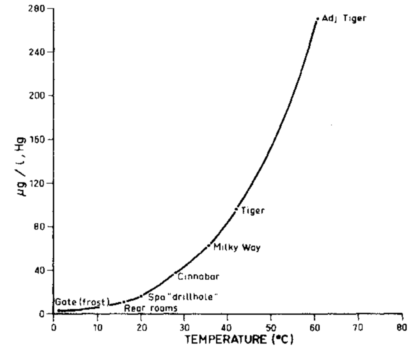

FIG.1.- The above points represent temperature and mercury concentration of thermal gases. The names are those of various balneal pools, or the approximate location. Gate (frost) refers to a sample collected from a small vent near the gate at the rear of the Spa hotel leading to the Tiger bath when the ground was covered in frost. Rear rooms' vent is at the south west corner of the Spa's western building; the Spa 'drillhole' is similarly located on the eastern building.

two days (max.) required at Ngawha during rain.

The standard electrode potentials are:

$$Hg^{++} + 2e^- \rightarrow Hg \quad + 0.851V \ (\varepsilon^o) \text{ and}$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O + 1.229V \ (\varepsilon^o)$$

Thus the reaction $2Hg + 4H^+ + O_2 \rightarrow 2Hg^{++} + 2H_2O$ is thermodynamically spontaneous, the standard e.m.f. being $\varepsilon^o = + 0.378V$.

The favoured 'mechanism' of transport deposition from alkaline sulphide solution (Krauskopf, 1951) is impossible in this case. There are no ascending waters and all waters present are acidic to almost neutral. The other major defect with the alkaline sulphide hypothesis is that it is cyclic. It assumes the pre-existence of cinnabar. Colloidal transport (Dickson and Tunell, 1968) is unlikely, as borehole waters (near the Ngawha Springs Hotel) contain only 0.00007 ppm total Hg, whilst surface waters, even in areas depositing cinnabar, have less than 0.03 ppm total Hg, all of which is elemental mercury.

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