Precious metals in ferromanganese crusts from the south-west Pacific

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Little is known about the abundance, distribution and origin of the precious metals in marine ferromanganese materials[1-4], although it has long been recognized that elements such as silver and gold are frequently enriched in ferromanganese nodules when compared with average crustal abundance[5]. Relative to crustal abundance, silver is enriched in nodules[5] by a factor of between 50 and 100, and for gold enrichment factors of between 100 and 1,000 have been found[3]. We know of no similar data in the literature for silver and gold in ferromanganese crusts, although Halbach et al.[4] have described enrichment of platinum in crusts from the central Pacific region. Elsewhere, precious metals show significant enrichment, possibly to economic grades, in massive sulphide deposits associated with active spreading centres such as the East Pacific Rise and the Red Sea[6-8]. We now report an unusual occurrence of silver and gold in ferromanganese crusts from a back-arc setting in the south-west Pacific; to our knowledge, the first report of material of this kind.

The ferromanganese crust samples described here were collected from several widely spaced sites on the northeastern and eastern margins of the Indo-Australia Plate (Fig. 1, Table 1). The northernmost deposit (SP10) occurs on the flanks of the South Rennell Trough, situated between the Solomon Islands and New Caledonia, and interpreted by Larue et al.[9] as an Oligocene spreading zone. Sample SP29 is from the north-west margin of the Reinga Basin on the eastern flank of the Norfolk ridge. Sample SP40 is from the eastern flank of the Loyalty Island chain between New Caledonia and Vanuatu. The Loyalty Islands are interpreted by Parrot and Dugas[10] to be the volcanic arc linked to an Eocene to early Oligocene, north-east-dipping subduction zone bordering the Norfolk Ridge. Samples were collected by dredging during the GEORSTOM III NORD (September 1975), ORSTOM EVA I (April–May 1976) and GEORSTOM III SUD (January 1983) cruises, from water depths ranging from 900 to 3,650 m.

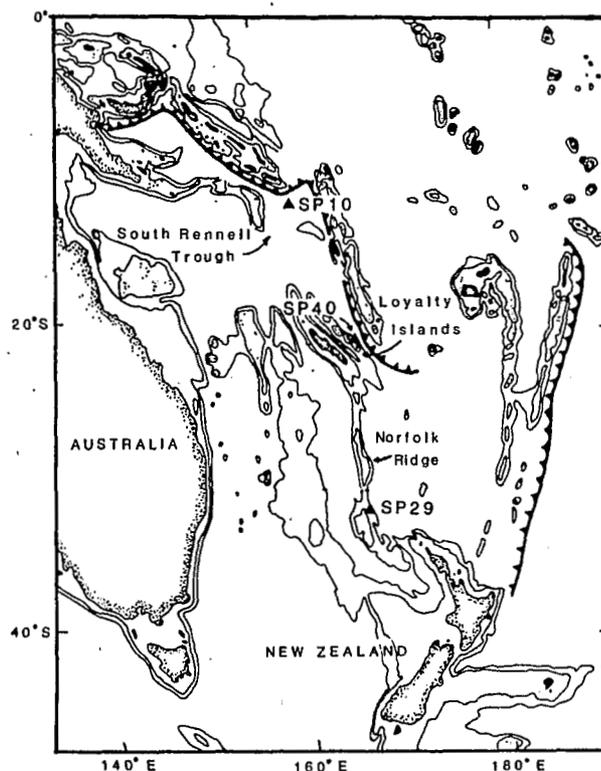Ferromanganese crusts examined here vary considerably in

Fig. 1 Map showing location of samples, 1,000- and 2,000-m contours and position of trenches.

surface texture and internal structure. Sample SP10, which is up to 3 cm thick, consists of a slightly gritty and mamillated surface layer with patches of adhering clay, underlain by brownish-black, porous and unlayered ferromanganese material. The substrate for this crust is variably altered basalt, which is separated from the crust by a thin (<1 mm), discontinuous layer of white clay. Crust SP29 consists of a hard, dense and smooth outer layer over black, crudely layered and hard ferromanganese material up to 3 cm thick. The substrate for this crust is bluish-grey chert and chert breccia. Sample SP40 has a rough, gritty surface texture and is composed of brownish-black, coarsely layered ferromanganese material up to 2.5 cm thick. Layering, which occurs on a centimetre scale, is, in part, defined by a higher proportion of light-coloured detrital material in the outermost part of the crust; layers also show a very fine internal lamination, usually <1 mm thick. This crust overlies a mottled, brown to white, gritty clay. The presence of relict pyroxene, magnetite and apatite suggests that this material is probably degraded tholeiitic basalt. Feldspars have generally weathered to clays and recrystallized to phillipsite.

Under high magnification, all crusts studied show features similar to those described for crusts elsewhere[6,11,12]. The dominant internal structure is a well-defined lamination which frequently forms branching or single digitate columns which may extend through the entire thickness of the crust and are usually perpendicular to the underlying substrate. Cavities between the columns may be filled with clay and entrapped protozoa, usually foraminifera.

Sub-samples of each of the three crusts were analysed by X-ray fluorescence, atomic absorption spectrophotometry, optical microscopy, scanning electron microscopy, X-ray diffractometry, Fourier-transform infrared spectroscopy and Mossbauer spectroscopy. Mineralogically, the crusts are remarkably uniform and consist essentially of X-ray-amorphous ferromanganese material. The only crystalline manganese oxide phase identified in the specimens is ferruginous vernadite, a

Table 1 Bulk chemical composition of crusts from the south-west Pacific* (all analyses in p.p.m. except where stated)

	SP10	SP29	SP40
Latitude	12° 00′ S	31° 52′ S	20° 47′ S
Longitude	162° 43′ E	168° 17′ E	167° 31′ E
Depth (m)	3,100–3,650	900–2,500	1,400–1,700
% Mn	14.8	20.9	14.9
% Fe	16	13.1	16.1
Pb	579	1,573	1,143
Ni	2,329	4,453	2,414
Cu	853	573	1,229
Zn	391	624	539
Co	1,560	6,350	3,720
Mineralogy	Vernadite	Vernadite	Vernadite

* Pb, Ni, Cu and Zn were analysed by X-ray fluorescence using air-dried samples; Mn, Fe and Co were analysed using atomic absorption methods.
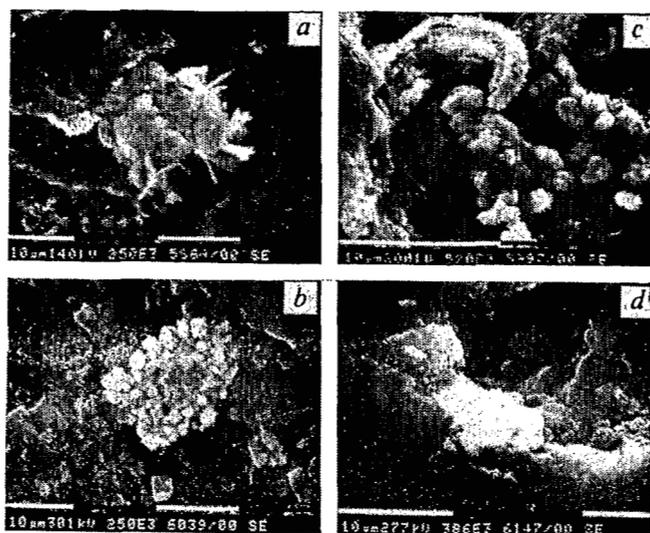
Fig. 2 Scanning electron micrographs of a, native silver, centre of field, bordered by radiating crystallites of acanthite; b, blocky argentite crystals in clay; c, curved particles of cerargyrite (top left) and blocky crystallites of argentite; and d, particle of gold, centre of field, in clay. White scale bar, 10 μm in each micrograph.

Fig. 3 X-ray energy spectra for a, silver sulphide in clay; b, silver chloride in clay; c, native gold in clay; d, bismuth chloride in clay; e, cassiterite in clay; and f, zinc–iron oxide mineral.

highly hydrated and very-fine-grained iron and manganese oxide[13,14].

The results of chemical analysis are given in Table 1. Preliminary analysis for Ag, Au and Pt shows concentration levels below the detection limit for the techniques used (1, 0.05 and 0.25 p.p.m. (parts per 10^6) respectively). A detailed report on crust mineralogy, chemistry and petrology is in preparation.

Analysis of samples using a scanning electron microscope fitted with an energy-dispersive X-ray system has identified particles of Ag and Au. Silver occurs in a variety of forms, including native silver, silver chloride, a radiating, platy silver sulphide, and an unusual blocky silver sulphide (Fig. 2). Characteristic X-ray energy spectra for the precious metal compounds identified in this study are presented in Fig. 3.

Grains of native silver, the most common variety detected, typically occur in discrete scale-like crystals, irregular in outline and ranging in size from 5 to 50 μm (Fig. 2a). The radiating platy silver sulphide has been tentatively identified as acanthite (Ag_2S), on the basis of crystal morphology (Fig. 2a). This typically develops as crusts on particles of native silver. A second, blocky silver sulphide (Fig. 2b) has been similarly tentatively identified as argentite. This usually occurs as sub-micrometre-sized crystals, often apparently cubic and octahedral, growing from the clay matrix. The silver chloride mineral (Fig. 2c) had a very distinctive morphology, consisting of curved particles, suggesting horn silver or ceragyrite (AgCl). This is rarer than the sulphides, and has been observed chiefly on a clay substrate. From 185 silver-containing grains identified by X-ray energy spectroscopy, 143 were native silver, 30 were silver sulphides, and 12 were silver chloride.

Gold, rare compared with silver particles in the samples studied, also occurs in its native form in grains irregular in shape and up to ~10 μm in size (Fig. 2d). Also found in crusts and associated with Ag and Au particles are rare grains of SnO_2 (cassiterite), $BiCl_2$ (mineralogy unknown at present), and an unidentified zinc–iron oxide.

All the above particles are typically found in the argillaceous infilling between the vernadite columns or associated with the decay products of substrate materials. Only rarely do grains appear to be incorporated in the ferruginous vernadite laminae of the columns during their growth.
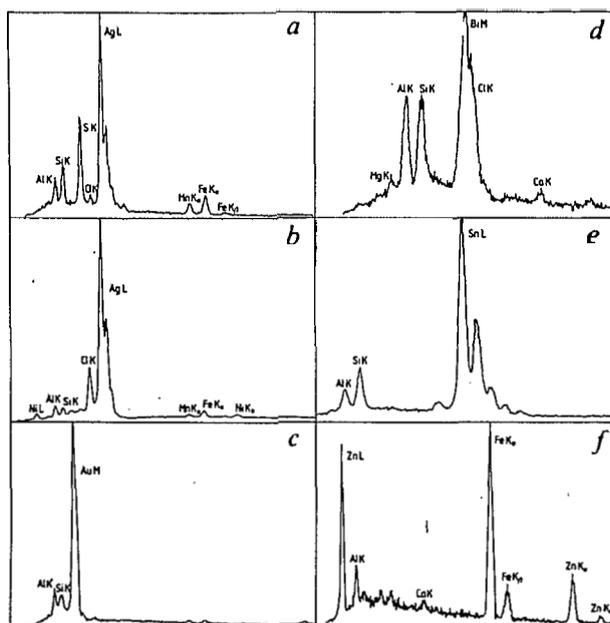
According to Cronan[5], major factors affecting rare-element enrichments in nodules and crusts include the adsorptive and crystallochemical characteristics of the ferromanganese oxides themselves, the rate of supply of the elements to the marine environment, their availability at the reaction site, and the nature of the environment of deposition. We have insufficient data to provide a detailed account of the distribution and origin of precious metals in the ferromanganese deposits studied here; however, absorption and substitution are unlikely to have played a major part in Ag and Au enrichment in crusts, as evidenced by the dominance of native metal forms associated with clays and, to a lesser extent, directly incorporated into manganese oxides.

With regard to the source of the elements, submarine volcanism has been seen[15-17] as responsible for the enrichment of some rare elements in nodules from volcanic areas. However, several factors would appear to suggest that submarine hydrothermal processes have not played a role in the growth of the crusts under investigation. First, the vernadite mineralogy of crusts is typical of ferromanganese deposits which have formed by hydrogenous processes, whereby growth is primarily the result of slow, inorganic precipitation of manganese oxides from the near-bottom water[4,6,18]. In contrast, hydrothermal manganese deposits from active spreading centres and other areas of submarine hydrothermal activity are frequently dominated by birnessite and todorokite[6,19]. Also, the approximately equal proportion of Mn and Fe and relatively high trace-metal contents in crusts, when compared with material formed by hydrothermal processes, is further evidence, together with their general appearance, that crusts probably have a hydrogenous origin[6,20]. Nowhere have we observed Ag to be in association with the Fe, Cu and Zn sulphide phases characteristic of hydrothermally derived massive sulphide deposits such as those that are known to occur on the East Pacific Rise[7].

Previous work on the influence of environmental controls on the distribution and enrichment of Ag in marine sediments has suggested that the most likely removal areas are in nearshore muds or other areas in which oxygen-depleted conditions are maintained. It has been suggested that in these areas Ag is precipitated as silver sulphide after initial supply to the sediment with accumulating organic carbon[21,22]. A similar mechanism of

enrichment has recently been suggested for Co in ferro-manganese crusts forming near areas where the oxygen minimum zone impinges on the flanks of some island chains and seamounts in the Pacific[23]. Although data are scarce, we find no convincing evidence for similar environmental controls acting on the crusts under study. Co concentrations are low (Table 1) compared with the crusts mentioned above, and the sediments associated with crusts show no signs of significant oxygen depletion, being bioturbated and light in colour.

The tendency for the Ag and Au particles examined here to occur in clays, either filling voids between vernadite columns or associated with degraded igneous substrate, suggests that at least some of the Ag and Au particles may be of detrital origin. This mode of origin is further supported by the generally irregular shape of the grains and the presence in at least one sample of native silver embedded in slightly altered basalt. However, the delicate, finely crystalline nature of some silver sulphide and chloride particles, together with their apparent intimate relationship to associated clays suggests an authigenic origin. Possible mechanisms for authigenic growth might include diagenetic remobilization and subsequent flocculation of silver colloids from the surrounding clays[3,24], or direct precipitation of Ag and Au chloro-complexes, the main species of these metals in the overlying sea water[25].

We suggest, therefore, that although the origin of Ag and Au particles in these crusts remains unclear, the major factor influencing their concentration appears to be the presence of a local, metal-enriched igneous source which on degradation has liberated particles of Ag and Au which have, in turn, been entrapped in overlying ferromanganese crusts and associated sediments. Susbsequent diagenetic remobilization of some of this Ag has apparently led to the development of authigenic sulphide and chloride phases.

To our knowledge these data represent the first report of particulate silver and gold in intimate association with ferro-manganese crusts. Their discovery may have important implications for the offshore resource potential in the south-west Pacific. If further work should locate additional material similar to that described above, and if grade and abundance criteria are met, this material may have economic value.

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Contribution of metabolic carbon to mollusc and barnacle shell carbonate

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Carbon in marine calcareous tests is not necessarily derived only from dissolved inorganic carbon (DIC) in ambient sea water; metabolic carbon can also be incorporated into carbonate tests, as shown by experiments using ^{14}C-labelled food during the incubation of sea urchin embryos and coral[1,2]. ^{14}C-rich organic matter (relative to seawater DIC) from terrestrial vegetation as well as marine organic matter (reflecting seawater DIC) is used as food by marine organisms in near-shore environments. This use provides the basis for a natural experiment on the systematics of metabolic carbon incorporation into carbonate tests. Here we have combined ^{14}C/^{12}C and ^{13}C/^{12}C ratio measurements on both the calcareous and the organic parts of marine organisms and on DIC, plankton and other carbon-bearing materials collected in and around New Haven Harbor (Connecticut, USA) in Long Island Sound, where the various sources of carbon can be identified, and we deduce that a large percentage of the carbon in calcareous tests is metabolic carbon. Thus, it is at best difficult to use the δ^{13}C values of ancient biogenic carbonate from molluscs to predict the ancient δ^{13}C values of seawater DIC.

Living barnacles and a variety of molluscs were collected during the period 1983–85 at three sites in New Haven Harbor (see Fig. 1). During the same period sea water, sediment, sea-
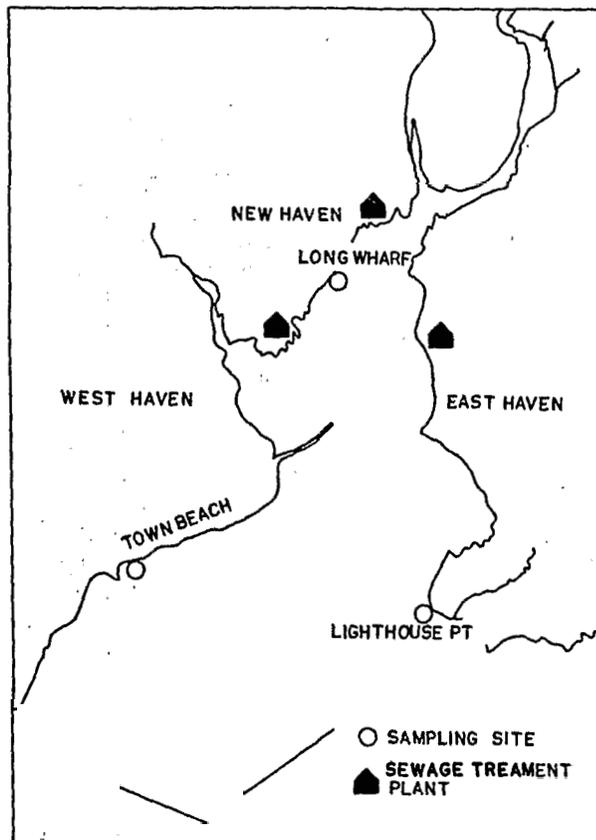

Fig. 1 Sampling sites in New Haven Harbor. The three municipal sewage treatment plants located inside the harbour are indicated.

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