

solution. The resultant precipitate of ferric hydroxide, which carried down more than 97 per cent of the germanium present in the sea-water, was dissolved in concentrated hydrochloric acid. Germanium was extracted from the acid solution with carbon tetrachloride, back-extracted with water and determined spectrophotometrically with phenylfluorone.

Surface samples of water from the Irish Sea (2), the English Channel (4) and the North Atlantic (2) were found to contain 0.06 ± 0.01 $\mu\text{gm.}$ of germanium/kgm. (0.82 ± 0.13 $\mu\text{gm.}$ -atom/ton). Samples taken at depths of 240–270 m. and 3,660–3,900 m. at lat. $47^\circ 47' \text{N.}$, long. $9^\circ 18' \text{W.}$, contained 0.06 and 0.07 $\mu\text{gm.}/\text{kgm.}$ (0.82 and 0.96 $\mu\text{gm.}$ -atom/ton) respectively. The average germanium concentration found is of the same order as that predicted by Ishibashi and Shigematsu⁵. Germanium is concentrated in sea-water, relative to the closely related element silicon, having a silicon : germanium ratio of about 17,000 : 1 (assuming a silicon concentration of 1,000 $\mu\text{gm.}$ silicon/l., which is probably considerably higher than average); compared with a ratio of about 140,000 : 1 in the lithosphere. The concentration of the element in sea-water is much more constant than that of silicon, which varies⁶ over the range 10–2,500 $\mu\text{gm.}/\text{kgm.}$ This constancy is probably attributable to the fact that, unlike silicon, it is not utilized appreciably by plankton.

Further work is in progress on the marine geochemistry of germanium.

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Gallium

LITTLE is known of the occurrence of gallium in sea-water. Its presence was first detected by del Campo and Rodeja¹. Bardet *et al.*² found it spectrographically, together with thirteen other trace elements, in water samples taken near Roscoff (Brittany). The only quantitative data so far published are due to Noddack and Noddack³, who found 0.5 $\mu\text{gm.}$ of gallium/l. in the water of Gullmars Fjord, Göteborg, Sweden; this analysis can scarcely be considered representative of ocean water, since the sample was taken from a fjord which is likely to be contaminated by drainage from the land. Ishibashi and Shigematsu⁴ have predicted the abundance of gallium in sea-water to be 0.005 $\mu\text{gm.}/\text{l.}$

The present communication records an attempt to obtain quantitative data on the occurrence of gallium in sea-water. The element was precipitated in 93 ± 5 per cent yield from 5-l. samples of filtered sea-water using ferric hydroxide as carrier. The ferric hydroxide precipitate was dissolved in hydrochloric acid, titanous chloride was added to reduce the iron to the ferrous state, and gallium was then extracted with di-*iso*-propyl ether. After evaporation of the ether, gallium was determined spectrophotometrically in the residue, using a modification⁵ of the rhodamine B method of Onishi and Sandell⁶.

Samples of the surface waters of the Irish Sea (4), the English Channel (1), and North Atlantic (2) contained 0.030 ± 0.007 $\mu\text{gm.}$ gallium/kgm. ($0.43 \pm$

0.10 $\mu\text{gm.}$ -atom/ton). Two samples taken at depths of 240–270 m. and 3,660–3,900 m. at lat. $47^\circ 47' \text{N.}$, long. $9^\circ 18' \text{W.}$ contained 0.037 and 0.023 $\mu\text{gm.}$ gallium/kgm. (0.53 and 0.33 $\mu\text{gm.}$ -atom/ton) respectively. It is not considered that these variations are significant, since they are of the same order as the analytical error. The average gallium content of sea-water is thus about 0.03 $\mu\text{gm.}/\text{kgm.}$ —a value very much less than that found spectrographically by the Noddacks, but more in line with the relative abundance of the element in the lithosphere.

Further work on the occurrence of gallium in marine organisms and sediments is in progress.

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'Sub-Grains' and Etch Figures in Lead

IN the course of a recent investigation into the ageing characteristics of lead-antimony alloys¹, microscopical examinations of a range of aged specimens were carried out and recrystallized areas were observed in a number of the specimens which had been strained prior to ageing. The specimens had been prepared by the normal metallographic techniques of grinding and polishing and had been etched in Worner and Worner's reagent² to disclose the extent of precipitation. In a number of the specimens the precipitated antimony was cleared from the surface by a brief immersion in concentrated nitric acid (s.g. 1.42) and subsequent examinations showed the recrystallized areas to be covered with networks of fine lines producing an appearance of sub-grains, similar to that due to polygonization, which had been absent from the specimens prior to the nitric acid treatment.

Specimens of unalloyed lead which were given the same etching treatment were found to show this structure over their entire surfaces even in cast material, and modifications in straining and annealing procedure did not produce changes in sub-grain dimensions. Repeatedly re-etching the same area of a single specimen did not develop the same configuration of sub-grains, and it was concluded that the network of lines did not result from the structure of the lead but was an effect produced primarily by the action of the nitric acid.

The effects of etching treatments in a range of concentrations of nitric acid on prepared specimens of annealed, unalloyed lead were then observed and it was seen that the 'sub-grain' dimensions increased with the degree of dilution of the nitric acid (see Figs. 1 a and b). At 20 per cent dilution a mottling of the surface had started to spread from the 'sub-grain' boundaries and at 30 per cent dilution the entire surface was mottled and etch figures had started to form within the 'sub-grains' (see Fig. 1 c). These etch figures continued to develop to the extent shown in Fig. 1 d by treatment in nitric acid diluted 40 per cent.