PAPERS AND PROCEEDINGS OF THE ROYAL SOCIETY OF TASMANIA, VOLUME 88

Note on the Occurrence of Trace Elements in Clays of the Huon District

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ABSTRACT

Samples of clays from localities in the Huon district were found to contain traces of nickel, copper, zinc, molybdenum, manganese and relatively large amounts of vanadium.

INTRODUCTION

Clays, consisting mainly of kaolinite were collected from the clay pit at Surges Bay, the foreshore of Killala Bay and the Granton Brick Company's clay pit at Dover. The clay from Surges Bay was formed by weathering of a syenite dyke and the Killala clay was formed by the weathering of the Ferntree Mudstone. The Dover clay was formed partly by weathering of Permian rocks and also by transportation and deposition of clay material from elsewhere. The elements were determined using colorimetric methods of estimation as given by Sandell (1950). The colours were developed and compared with standard graphs constructed using an E.E.L. photometric colorimeter. Elements sought in the investigation were copper, nickel, zinc, cobalt, lead, cadmium, chromium, molybdenum, manganese and vanadium. The study was suggested by Prof. S. W. Carey and carried out using equipment from the Chemistry Dept. by courtesy of Prof. E. E. Kurth. The amount of sample analysed was 0·5 gm. of dried clay. However, it was noticed that samples absorbed water during weighing.

Results of analyses

Copper, zinc, lead, and cadmium were estimated by comparing the colours of their dithizonates with standards. Cobalt and nickel were concentrated using dithizone. The blue colour of the cobalt thiocyanate complex was used for cobalt, and nickel was determined using the colour of the dimethylglyoxime complex. In the above estimations the samples were decomposed using perchloric and hydrofluoric acids. Sodium carbonate fusions were used to break down the samples for the determination of chromium, molybdenum, manganese, and vanadium. Di-phenylcarbazide was used to produce a chromium complex, ammonium thiocyanate and stannous chloride for molybdenum, potassium periodate for manganese, and vanadium was measured using the colour of phosphotungstovanadic acid after extraction with 8-hydroxyquinoline.

TABLE OF TRACE ELEMENTS FOUND IN HUON CLAYS
(in parts per million)

	Dover	Surges Bay	Killala
Cobalt	<10	<10	<10
Nickel	28–32	20–23	26–30
Copper	11–12	16	<1
Lead	<1	<1	<1
Zinc	20–24	28–30	17–19
Cadmium	<1	<1	<1
Chromium	<1	<1	<1
Molybdenum	4	6–8	14–15
Manganese	15–16	not found	trace
Vanadium	435–440	180–200	497–500

Where the amount is listed as less than a specified amount, it means that no reaction was found, when the sensitivity of the test was the specified amount.

Origin of trace elements

The origin of the trace elements is of interest. With the exception of vanadium and molybdenum the trace elements appear in lower concentrations than expected when compared with clay samples from other parts of the world. The concentration of nickel relative to cobalt is apparently due to the lack of iron in the clays, the latter usually being associated with iron in the geochemical cycle. The nickel concentration is similar to that found in non-ferrous aluminium-rich sediments. The actual origin of the nickel may be from small mineral fragments found in the clays. The variation of copper suggests that it is present as mineral fragments rather than as part of the clay mineral structure. Rankama and Sahama (1950) state that copper occurs in aluminous sediments by absorption. Green (1953) gives the average concentration of copper in shales as 192 ppm. The concentration of the copper is very much lower than average.

The concentration of zinc is low in all clays examined. It is possible for zinc to occur in the clay mineral structure by replacement of aluminium. This does not occur with pure kaolinite type clays. The zinc ion is very mobile in weathering processes hence it may have been largely leached from the clay materials. The greatest amount of zinc occurs at Surges Bay where it may have originated from the ferro-magnesian minerals of the syenite. Molybdenum is present in larger quantities than expected. Molybdenum is enriched in carbonaceous sediments. Its high concentration at Killala Bay may be due to the presence of numerous carbonaceous remains in the Permian rocks from which it was formed. The manganese has been leached from the clays by weathering processes hence not much was found in the analyses.

The high concentration of vanadium is interesting. During weathering processes vanadium is incorporated in clay minerals, by replacement of aluminium. The vanadium in the samples was also found to be concentrated in the clays and not in the silt fractions. It has been found that vanadium is enriched in carbonaceous sediments. The Permian mudstones from which the Killala clay has been formed, contain many carbonaceous markings and remains of fossil wood. Carbonaceous remains also occur in the residual clay deposit at Dover. It is considered that the vanadium was derived from these and ultimately became incorporated in the clay by subsequent weathering processes. The transported clay at Dover has been considered to have been derived by weathering of dolerite which may contain appreciable traces of vanadium, Green (1953) considers that igneous rocks average 150 ppm. vanadium. The Surges Bay clay has less vanadium than the other deposits. The metal here could have come from ferro-magnesian minerals and apatite in the syenite. Vanadium can occur in apatite with V^{5+} replacing P^{5+}. Syenite generally contains about 30 ppm. vanadium.

Where high concentrations of vanadium are present the vanadium comes to the surface as a yellow-brown stain which becomes green on exposure to the air. This stain is common on Permian rocks in the area. Bricks made from the clay become green on exposure. Treatment of the green stain with dilute hydrochloric acid produces an orange precipitate which is soluble in the acid. If ammonia is used the green stain becomes blue and subsequently dissolves. It is suggested that an acid or alkali washing plant may be useful in removing vanadium from the clay. The vanadium however may not be released chemically until after firing in the kiln.

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