

magnetic curves were observed for all samples from North Head. An initial Curie temperature of between 300 and 400 °C was followed by an increase in magnetisation and a subsequent final Curie point between 500 and 580 °C. The saturation magnetisation after thermal cycling was always greater than the initial saturation magnetisation. This type of irreversible thermomagnetic behaviour has been observed in dredged pillow lavas⁷ and in DSDP basalts^{8,9}. The thermomagnetic results—and microprobe examinations of the opaque minerals (R. F. B., S. K. B. and J. H. S., unpublished)—indicate that the magnetic minerals in the North Head samples are non-stoichiometric titanomaghaemite. These cation-deficient phases are the products of low temperature oxidation resulting from prolonged seafloor weathering of the late Tertiary oceanic pillow basalts.

All of the Langdon Point samples show reversible thermomagnetic curves with a single Curie temperature very near 580 °C, indicating that the magnetic mineral in these metamorphosed pillow lavas is magnetite containing little or no titanium. Reversible thermomagnetic curves indicating Curie points of 580 °C have not been observed previously in analyses of dredged pillow basalts or DSDP basalts. This 'unusual' behaviour is almost certainly the result of burial metamorphism undergone by the Langdon Point basalts. The fine-grained titanomagnetites in young dredged pillow basalts are known to be very susceptible to chemical change when heated. At any significant depth in the oceanic crust pillow basalts would be exposed to heating by the intrusion of feeder dykes leading to overlying pillow lavas, the emplacement of underlying sheeted dyke and plutonic complexes, or even by exothermic hydration reactions within the metamorphosed pillow lavas themselves². Thus, the metamorphosed pillow lavas from Langdon Point and their resulting magnetic properties are thought to be the natural consequence of burial metamorphism experienced during seafloor spreading by basalts at significant ($> 1/2$ km?) depths in the oceanic crust.

The evidence from DSDP basalts, and the data presented here on pillow lavas from the North Head region of Macquarie Island indicate that the progressive submarine weathering of the oceanic crust decreases the NRM intensity of the upper portion of oceanic crust to $\sim 10^{-3}$ gauss. Lowrie, *et al.*⁸ have suggested that the 10^{-3} gauss NRM intensities of DSDP basalts are perhaps only representative of the strongly weathered zone at the top of the pillow lava layer and that unweathered pillow lavas below the weathered zone may be more strongly magnetised. But if the pillow lavas from Langdon Point on Macquarie Island are representative of pillow basalts from depths of 500–1000 m, the NRM intensity of these deeper extrusives would also be of the order of 10^{-3} gauss. Since a 1-km thick layer of pillow basalts magnetised at 10^{-3} gauss is not sufficient to yield the observed amplitude of marine magnetic anomalies, we conclude that the underlying basaltic and doleritic sheeted dyke complexes also contribute to the anomalies. Detailed analysis of changes in marine magnetic anomaly profiles with age of the underlying oceanic crust has led to a similar conclusion (R. J. Blakely, unpublished).

We thank Dr R. I. Garrod, Director of Antarctic Division, Australian Department of Science, and Dr R. Varne for assistance throughout this project. Assistance during field work was given by P. Williamson and P. J. Gloag; many of the sample measurements were done by Dave Bodgan and Jim Mellema. This project was funded by the National Science Foundation.

ROBERT F. BUTLER

Department of Geosciences,
University of Arizona,
Tucson, Arizona 85721

SUBIR K. BANERJEE
JAMES H. STOUT

Department of Geology and Geophysics,
University of Minnesota,
Minneapolis, Minnesota 55455

Received June 23; accepted August 15, 1975.

- ¹ Banerjee, S. K., Butler, R. F., and Stout, J. H., *Z. Geophys.*, **40**, 537–548 (1974).
- ² Varne, R., and Rubenach, M. J., *Antarct. Res. Ser. (Am. geophys. Un.)*, **19**, 251–266 (1972).
- ³ Williamson, P., *Bull. Aust. Soc. Explor. Geophys.*, **5**, 19–21 (1974).
- ⁴ Talwani, M., Windisch, C. C., and Langseth, M. G., Jr., *J. geophys. Res.*, **76**, 473–517 (1971).
- ⁵ Atwater, T., and Mudie, J. D., *J. geophys. Res.*, **78**, 8665–8686 (1973).
- ⁶ Irving, E., *Can. J. Earth Sci.*, **7**, 1528–1538 (1970).
- ⁷ Marshall, M., and Cox, A., *J. geophys. Res.*, **77**, 6459–6469 (1972).
- ⁸ Lowrie, W., Løvlie, R., and Opdyke, N. D., *Earth planet. Sci. Lett.*, **17**, 338–349 (1973).
- ⁹ Lowrie, W., Løvlie, R., and Opdyke, N. D., *J. geophys. Res.*, **78**, 7647–7660 (1973).

Effect of oxygen on aldolisation reactions

ALTHOUGH the kinetics of aldolisation reactions have been studied^{1,2}, no observations have been reported concerning the effect of oxygen on their rates and kinetics. We have studied polarographically the aldolisation of acetaldehyde in 1 M lithium hydroxide in the absence of oxygen and spectrophotometrically in the presence of air using absorbance at 230 and 277 nm. A difference in the concentration–time curves obtained using these two procedures was observed.

The base-catalysed autoxidation of ketones is probably³ initiated by the interaction of molecular oxygen with carbanions formed in alkaline media and in the past the observed discrepancy has, therefore, been attributed to the interaction of atmospheric oxygen with carbanions formed as intermediates in the course of aldolisation.

To test this hypothesis, we studied reactions of α -phenyl-substituted aldehydes of the type $\text{RCH}(\text{C}_6\text{H}_5)\text{CHO}$ in alkaline media. The pK values of these compounds⁴ are such that they exist in 1 M lithium hydroxide almost completely in the carbanion form. Observations of these compounds during kinetic runs showed that they behaved differently in the presence and absence of oxygen. In the absence of oxygen, polarographic and spectrophotometric measurements gave identical rates. As a side product of the reactions RCOC_6H_5 compounds are formed in the presence of air⁵, further confirming the reaction of carbanion with oxygen. The latter reaction has also been postulated as a side product of the oxidation of phenylacetaldehyde to benzoic acid⁶ and in association with the alkaline rearrangement of aconitine⁷.

Thus some discrepancies reported for the kinetics of aldolisation may result from an interaction between molecular oxygen and the carbanion intermediate. Consequently, in future studies of aldolisation and other reactions which involve carbanion formation, oxygen should be excluded completely.

D. BARNES

Department of Civil Engineering,
University of Strathclyde,
Glasgow, UK

P. ZUMAN

Department of Chemistry,
Clarkson College of Technology,
Potsdam, New York 13676

Received July 28; accepted August 8, 1975.

- ¹ Anderson, J. B., and Peters, M. S., *J. chem. Engng Data*, **5**, 359 (1960).
- ² Bell, R. P., and McTigue, P. T., *J. chem. Soc.*, 2983 (1960).
- ³ Wallace, T. J., Pobiner, H., and Schriesheim, A., *J. org. Chem.*, **30**, 3768 (1965).
- ⁴ Barnes, D., and Zuman, P., *J. electroanal. Chem.*, **46**, 343 (1973).
- ⁵ Barnes, D., and Zuman, P., *J. chem. Soc., Perkin Trans.* (in the press).
- ⁶ Doering, W. von E., and Haines, R. M., *J. Am. chem. Soc.*, **76**, 482 (1954).
- ⁷ Wiesner, K., Gotz, M., Simmons, D. L., and Fowler, L. R., *Colln. Czech. chem. Commun., Engl. Edn*, **28**, 2462 (1963).