Fig. 3. Electron micrograph of lightly etched surface of a 'crystalline' precious opal from Tintenbar, New South Wales. Surface etched with hydrofluoric acid. (Carbon replica, chromium-shadowed)

quently form colloidal spheres capable of enlargement, flocculation, and deposition as opaline silica gel in the presence of a sufficient concentration of electrolytes.

Silicification of certain horizons is characteristic of many Australian lateritic profiles⁷, and the major opal deposits are associated with such profiles. It is noteworthy, therefore, that abundant sulphates occur in the environment of opal deposition. Examples of this are the occurrence of gypsum at Andamooka, South Australia; gypsum and alunite at Coober Pedy, South Australia; gypsum and glauberite at White Cliffs, New South Wales; and alunite at Lightning Ridge, New South Wales.

These observations do not imply that all precious opals are formed by weathering processes. Precious opal from Tintenbar, New South Wales, occurs in amygdaloids in decomposed basaltic rocks, which may imply a hydrothermal or deuteric origin⁸. This material shows the characteristic regular particulate structure¹ (Fig. 3) of a precious opal, but is exceptional in that it is moderately crystalline (disordered tridymite-cristobalite). Other samples of precious opal associated with volcanic rocks, however (as at Rocky Bridge, New South Wales; Springsure, Queensland), yield only the customary near-amorphous type of diffraction pattern.

We thank Dr. M. J. Ridge for helpful suggestions and advice and Dr. R. Inman for assistance in the electron microscopy.

J. B. JONES
J. BIDDLE

Department of Geology and Mineralogy,
University of Adelaide, South Australia.

E. R. SEGNI

C.S.I.R.O.
Division of Building Research,
Melbourne, Australia.

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CHEMISTRY

Differential Thermal Analysis of Thallous Azide

In their review of inorganic azides, Evans, Yoffe and Gray¹ note that the crystal structure of thallium azide is body-centred tetragonal and that the compound melts with decomposition at about 334° C. On differential thermal analysis, a solid-state transition is shown before

Fig. 1. Differential thermal analysis of thallium azide (A) and its decomposition product (B)

the fusion process. As shown in Fig. 1A this transition has a maximum peak temperature at 291° C. If the sample is allowed to undergo a cooling cycle before decomposition sets in, then the transition is seen to be reversible. Fig. 1A, however, takes the sample through the decomposition process. The exothermic peak is caused by oxidation of the azide group to molecular nitrogen. Thallium metal is the other product of the thermal decomposition and Fig. 1B shows the hexagonal-cubic transition near 234° C, previously reported by Mazières², followed by melting at 299° C.

The DuPont 900 differential thermal analyser, provided with an aluminium heating block and chromel alumel thermocouples, was used to obtain the thermogram. Approximately 3 mg of azide sample, contained in a glass capillary tube, was run in air against glass beads as a reference material. The heating rate was 20° C/min. The sample of thallous azide powder was prepared by precipitation from a mixture of ethanolic solutions of thallous acetate and sodium azide.

O. F. KEZER
H. ROSENWASSER

Basic Research Laboratory,
U.S. Army Engineer Research and
Development Laboratories,
Fort Belvoir, Virginia.

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Radiolysis of Nitroalkanes

Few investigations of the radiolysis of nitroalkanes have been reported¹ and, apart from the use of tetranitromethane as a scavenger in aqueous solutions², no systematic study of their radiation chemistry has been made. The liquids are highly polar and ionic reactions might be expected to play a significant part in the decomposition processes. In order to obtain information on this problem we have examined the radiation chemistry of nitromethane, nitroethane, 1- and 2-nitropropanes, the first in considerable detail. Some of the salient features of this investigation are reported here.

Nitromethane was prepared by the reaction of monochloroacetic acid and sodium nitrite and purified by fractional distillation. Nitroethane and the nitropropanes were purified by fractional distillation under reduced pressure after alkali and acid washing. The irradiations were carried out with γ -rays from a cobalt-60 source using dose rates between 0.5 and 2.5×10^4 rads h⁻¹. Higher dose rates up