

direct radiation in the higher ozonosphere, though this is likely to be small, and changes in the circulation above 25 km induced by sudden heating.

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CERAMICS

Differential Thermal and X-Ray Analysis of Opal

PUBLISHED differential thermal analysis curves of opal show a marked rounded endotherm with the peak near 130° C, although one example shows a very small peak at this temperature¹. Curves we have obtained from the differential thermal analysis of some thirty naturally occurring opaline silicas can be broadly classified into three groups with: (1) a very small, or no apparent endotherm between 100° C and 200° C; (2) a prominent rounded endotherm starting at about 90°, with a peak temperature in the range 125°–140° C; (3) a strong, sharp endotherm, starting at 90° C, with a peak temperature of 140° C.

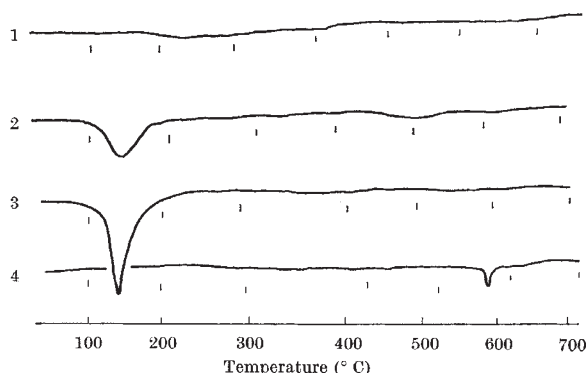


Fig. 1. Differential thermal analysis of opal and quartz. 1, Milky opal, White Cliffs, New South Wales; 2, brown common opal, Sunbury, Victoria; 3, brown opal, locality unknown; 4, quartz, run at the same sensitivity as the opals

Typical traces are shown in Fig. 1. Most glassy opals (including precious varieties) fell into group (1); opals of group (2) were commonly opaque. Only two samples have been found in group (3) and these were somewhat glassy red and brown opals from different localities. They gave identical differential thermal analysis traces.

Thermal analysis at 50° C/h of typical samples of each group showed rates of weight loss corresponding to the nature of the differential thermal analysis peaks. Opals of group (1) were still losing water at 500° C; but those of group (3) were almost dehydrated by 200° C.

All samples were analysed for silica and water content (determined as loss on ignition) but no correlation was apparent between composition and differential thermal analysis results.

X-ray powder patterns of more than 100 samples from widely varying localities and occurrences were taken. In confirmation and extension of the findings of Flörke² and others³ these showed all gradations from essentially amorphous material, through disordered tridymite-cristobalite with or without quartz, to well-crystallized α -cristobalite. No correlation between degree of crystallinity and chemical data was apparent. All amorphous opals fell into differential thermal analysis group (1), but no such correlation could be made for crystalline opals. Three tentative generalizations can be made: (a) opals from any one occurrence, regardless of appearance, give

similar powder patterns; (b) most precious opals are near amorphous; (c) most hyalites are near amorphous.

Our results strongly indicate that most of the water is not chemically bound in opal. The manner in which the water is held is being further investigated by detailed thermal, X-ray, infra-red, and electron micrographic analysis.

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CHEMISTRY

Partial Differentiation, with Special Reference to Thermodynamics

THIS communication is based on the idea that certain difficulties in thermodynamics are the direct result of defects in the standard and indeed universal definition of a partial differential coefficient. A new definition is therefore proposed which is more correct and more helpful in thermodynamics and possibly in other branches of science.

For the purpose of exposition it will be sufficiently general to consider a differentiable function, z , of three variables, x_1, x_2, x_3 , and we write therefore:

$$z = f(x_1, x_2, x_3) \tag{1}$$

(although of course z is also variable, to avoid confusion in what follows the term variable is reserved for x_1, x_2, x_3). If now the variables of (1) are allowed to change and if these changes are sufficiently small dz will be given by a simple linear equation:

$$dz = a \cdot dx_1 + b \cdot dx_2 + c \cdot dx_3 \tag{2}$$

This follows because products of small quantities may be neglected.

According to the standard definition¹, the partial differential coefficient $\partial z / \partial x_1$ is simply the rate of change of z with respect to x_1 when the other variables, x_2, x_3 , are held constant, and it is obtained by the ordinary rules of differentiation on this assumption. Thus it follows that $\partial z / \partial x_1$ equals the limiting value of the coefficient a as $dx_2 \rightarrow 0$.

The new definition shifts the emphasis by defining the partial differentials directly as the coefficients, a, b, c of equation (2) for infinitesimal changes. We therefore have three defining equations of which the first is:

$$\partial z / \partial x_1 = a = \frac{dz - b \cdot dx_2 - c \cdot dx_3}{dx_1} \tag{3}$$

for infinitesimal changes. If there is only one variable, x_1 , a becomes the ordinary differential coefficient dz/dx_1 .

The advantages of the new definition are as follows:

(1) The new definition includes both ordinary and partial differential coefficients.

(2) The standard definition may give cause to error because although sufficient it is not entirely necessary. A glance at equations (2) or (3) shows that dz/dx_1 becomes equal to a whenever the sum $b \cdot dx_2 + c \cdot dx_3$ equals zero. This may happen in many ways besides making x_2 and x_3 constant.

(3) The new definition gives a better expression of the essential causative nature of the idea of partial differentiation. Equation (3) shows that $\partial z / \partial x_1$ is the rate of change of z with x_1 after correcting for the effects of the accompanying changes of the other variables. It is in fact the rate of change of z due to the change in x_1 alone.