Department of Mineralogy of the American Museum of Natural History.

GERALD M. FRIEDMAN

Department of Geology,
Rensselaer Polytechnic Institute,
Troy,
New York.

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MINERALOGY

Differential Thermal Analysis: Effect of Particle Size

SINCE differential thermal analysis involves the approach to equilibrium while the conditions are regularly changing (steady temperature increase), the recorded temperature of transformation depends on the reaction rate. This rate is affected by a catalyst. Rees[1] states that although the theory of catalytic action is only just being established, the dominant role of defects is generally accepted. More defects cause a decrease in the degree of crystallinity, which lowers the recorded temperature of transformation, as shown by the experimental results quoted by van der Marel[2].

One of the many defects tabulated in the first category of a review on the significance of solid state defects by Rees[1] is the discontinuity at a perfect surface. This surface is similar to that of a mosaic, which is an arrangement of sub-parallel blocks less than one micron in size. The fact that nearly all perfect-looking crystals contain sufficient defects to be idealized as a mosaic was deduced from the reduced intensities of the observed X-ray diffraction reflexions compared with the expected intensities from a perfect crystal. These deductions agree with my earlier results[3]. I observed that any particle size range greater than one micron gave a similar recorded temperature of transformation for a particular reaction.

Since the surface area is inversely proportional to the particle size, the less than ten milli-micron fraction, which has a greater surface area than a mosaic, will produce a decrease in the recorded temperature of transformation. In order to check the reduction in the recorded temperature of transformation, it is necessary to obtain fractions possessing identical other defects. However, the only available methods of fractionation and grinding have been shown to yield unsuitable material[3]. It is expected, therefore, that other defects in this size range would make the plane surface defect appear to be insignificant.

In conclusion, the recorded temperature of transformation is not affected by any particle size range greater than one micron, and is unlikely to be materially affected by a sub-micron size range.

Another type of structure, or an impurity, may affect the reaction rate. The accelerating catalysts are called activators or promoters, while those that decrease the reaction rate are called poisoners or depressants. The technique of annealing will remove many other types of structure and their associated effects on the reaction rate.

P. BAYLISS

School of Applied Geology,
University of New South Wales,
Sydney.

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OCEANOGRAPHY

High Interstitial Water Chlorinity in Estuarine Mangrove Swamps, Florida

RECENT investigations have shown that in coastal mangrove swamps of south-western Florida the average chlorinity of interstitial water contained in 2–4 ft. of unconsolidated sediment overlying bedrock is 2–12 parts per thousand greater than the average value of the overlying bottom water. General considerations would suggest that the two averages should be the same if chloride ions move across the sediment–water interface by molecular diffusion only.

During the rainy summer and autumn months these paralic swamps receive run-off from the extensive mainland swamps of southern Florida (Everglades) and consequently are flooded by fresh and brackish water of low chlorinity (0–15 parts per thousand). Throughout the following winter and spring drought months, marine water of normal (19 parts per thousand) to hyper-chlorinity invades the mangrove swamps. Submerged areas of the coastal swamps (excluding the mangrove forest) are typically 4–5 ft. deep at low tide[1].

The high interstitial water chlorinity observed in the sediments of these swamps was initially interpreted as a palaeochlorinity[2]. The results of this investigation, however, have established that the difference between the average sediment-water and bottom-water chlorinity is too large to be attributed to palaeochlorinities. In some back-swamp areas the difference is as much as 12 parts per thousand; the typical contrast is 6–7 parts per thousand. In general, the difference between the two averages increases with distance into the coastal swamps; the difference narrows as the mainland fresh-water swamps are approached. The large discrepancy rules out a palaeochlorinity interpretation because the sediment column is so thin (2–4 ft.) that any systematic decrease (or increase) in bottom-water chlorinity of the magnitude required would soon bring about similar changes in sediment-water chlorinity owing to ionic diffusion. Only if a dramatic decline in average bottom-water chlorinity had recently occurred could a palaeochlorinity interpretation be maintained. Chlorinity measurements during the past decade and the average bottom-water chlorinity estimated from the molluscan fauna of the surface sediment indicate that this instigating requirement has not occurred.

Anomalously high interstitial water chlorinity may also result from an *in situ* mechanism which retains chloride ions within the sediment. Such a mechanism, involving compactive dewatering of the sediment and the development of a clay-water system behaving as a semipermeable membrane, has been described by Siever *et al.*[3]. Deposits of the coastal mangrove swamps, however, are thin, essentially lack clay minerals, and, except for peat layers, have necessarily undergone little compaction. Many of the sediments are quartzose and shelly sands and coarse silts and accordingly are generally permeable; the necessary semipermeable membrane would therefore appear to be absent.

Digging animals may mechanically enrich surface sediment in relatively high-chlorinity water. Burrowing would in general be most active at times when the swamps are occupied by marine water. Biological turn-over of the sediment, or penetration of bottom water into the sediment mass along burrows, would therefore tend to cause the entrainment of water having a chlorinity considerably higher than the average value for the area. Arguing against this is the fact that the number of marine or euryhaline burrowing organisms found in areas of low average water chlorinity—the areas of maximum difference in average bottom-water chlorinity and sediment-water chlorinity—is quite small[4]. Thus digging organisms would appear to account for only localized enrichment of chloride ions in interstitial waters.