Nitrate and Ammonium Contents of Wisconsin Limestones

It has been suggested[1,2] that a number of environmental problems may be associated with high levels of nitrates and other nitrogenous compounds in waters. These problems relate to deleterious effects on human and animal health, crop quality and yields, and eutrophication of surface waters. Nitrate in the environment may be derived from nitrogenous fertilizers, organic wastes, soil organic matter, precipitation, and biologically fixed nitrogen. According to Feth[3], however, geological sources of nitrate have been largely ignored, and he has suggested that high levels of nitrate in water may be associated with limestones. We therefore measured the nitrate content of Wisconsin limestones.

Nitrate–nitrogen was determined in 210 limestone samples from quarries throughout Wisconsin. Major geological formations sampled were Niagara (Silurian), Galena Black River (Ordovician), Lower Magnesian (Ordovician), and Mendota (Cambrian) dolomites. Determinations were made with the nitrate-selective ion electrode following the procedure of Bremner, Bundy, and Agarwal[4], except that a 10 g sample (80-mesh) and 50 ml. of 0.01 M calcium sulphate were used. Nitrate–nitrogen and ammonium–nitrogen were also determined in seventy-four of these samples using the direct steam-distillation method of Keeney and Bremner[5]. Close agreement was found between nitrate–nitrogen values determined by the two procedures.

All samples contained measurable amounts of these forms of nitrogen, and values as high as 37 p.p.m. nitrate–nitrogen and 18 p.p.m. ammonium–nitrogen were obtained (Table 1). There seemed to be no relationship between nitrate content and type of limestone.

Table 1 Distribution of Nitrate—N[4] and Ammonium—N[5] in Limestone Samples

N content (p.p.m.)	Number of samples NO_3–N	NH_4–N
<2.5	135	49
2.6–5.0	48	15
5.1–7.5	8	6
7.6–10.0	9	3
10.1–15.0	5	0
15.1–20.0	3	1
20.1–25.0	1	0
>25.1	1	0
Total	210	74

Although ammonium nitrate is often used to blast limestone (about 1 kg per 5,000 kg rock), it undergoes decomposition to form nitrogen gas, nitrogen oxides and water, and contamination of samples by ammonium nitrate therefore seems unlikely. This was confirmed by analysing samples from a quarry adjacent to two recent blasts and from an area not blasted for 10 years. There was no difference in the nitrate or ammonium content of these samples (all less than 2 p.p.m. nitrogen), indicating that these forms were occluded within the rock.

Investigations involving the effect of grinding or of dissolving limestone in HCl showed that the nitrate and ammonium in limestones were present entirely as soluble salts. These forms of nitrogen are therefore retained by physical entrapment, and are released eventually on the weathering of the rock.

Although the nitrate and ammonium values obtained for a large number of samples seems relatively low (two-thirds contained less than 2.5 p.p.m. of each form), consideration of the amount of nitrogen in a layer of rock gives a different picture. For example, assuming an average density of 2.5 g per cm^3 for limestone, 1 p.p.m. of nitrogen is equivalent to 25 kg of nitrogen per hectare-metre. Several samples contained at least ten times this amount of nitrate–nitrogen.

Our results indicate that many limestones are a potential source of nitrate to percolate waters and that geological contributions of nitrate should be considered when evaluating sources of nitrate to ground waters.

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Subglacial Limestone Deposits in the Canadian Rocky Mountains

Ford *et al.*[1] have recently reported the discovery in the Rocky Mountains of Canada of calcite deposits which they have ascribed to a subglacial origin. The occurrence of such subglacial limestone deposits is, however, neither as rare in glaciated lands nor as neglected in the literature as they seem to believe. The problems of genesis noted by Ford *et al.* are therefore reviewed here in the context of a wider literature.

The first detailed discussion of deposits which are now considered to be subglacial limestone is probably that of Höeg[2], who supposed them to be postglacial marine deposits. The latest and most comprehensive study of subglacial limestone is that of Kers[3]. In addition to a historical review of the literature, Kers describes deposits of subglacial limestone from several new localities in Scandinavia. He concludes that the limestones were formed by the solutional and depositional agency of pressure meltwater at the ice sole; a conclusion which essentially follows a theory first advanced in 1936 by Ljungner[4].

In the account of Ford *et al.*, however, there seems to be an implicit assumption that the subglacial limestone deposits of the Mt Castleguard area were derived from free subglacial water. The agency of pressure meltwater is not considered. Yet pressure meltwater would seem to resolve the problems of genesis reported by Ford *et al.* The authors are puzzled because solute carbonate concentrations were found to be only small in the free meltwater streams of the Mt Castleguard area. But in the context of a pressure meltwater hypothesis, the chemical composition of these free meltwaters is not relevant. Similarly, the authors' assertion that "the environment" cannot be notably enriched in carbon dioxide is misplaced. The transposition of such "calcite precipitates" must require an agency rich in carbon dioxide and, indeed, there are strong grounds for supposing that the ice and pressure meltwater of the glacier sole would fulfil this requirement.

Corbel[5] has stressed the high concentration of carbon dioxide both in snow and snow-derived meltwater, and Williams[6] has shown that the carbon dioxide content of air within a snowbank may reach a concentration twice that in free air. Williams attributes this concentration of carbon dioxide to daily freezing and thawing at the surface of the snow. Freezing of meltwater releases the carbon dioxide it has absorbed from the atmosphere. Because it is a heavy gas, the carbon dioxide remains in the snowbank and rain or meltwater passing through can absorb the gas to the point of saturation. In this way the water is provided with carbonic acid for chemical weathering.