

process. The sediments deposited near the continental margins accumulate in great basins known as geosynclines. Much of the debris has been transported by water and has reacted with water and the atmosphere. Some is sandy material consisting of mineral grains relatively little changed by surface reactions. Minerals, such as quartz, and feldspars may make up much of such sands. More muddy materials may have a much larger contribution from materials produced by surface chemical reactions; minerals such as clays, chlorites, zeolites, etc. These minerals are characterized by very large water contents; they are among the most highly hydrated minerals known. At times, massive contributions to the sediment may arise from the accumulation of skeletal debris of living organisms. Thus in appropriate situations massive deposits of calcite and aragonite (both CaCO_3) may form. The importance of such activity of the oceanic biomass can be appreciated when one considers some parts of the European Alps where mountain ranges are dominated by this material. At other times deposits of amorphous silica result from the accumulation of radiolarian skeletons. These rocks are termed cherts. The same debris may also form parts of more normal muds. In some thick geosynclinal deposits such as those of the New Zealand Alps or the Coast Ranges of California, much of the debris is derived from volcanic activity. It consists of volcanic mineral grains mixed with minor amounts of weathered materials and carbonates. Not infrequently, submarine lavas may make a significant contribution. These can often be recognized by their so-called 'pillow structure'. These same lumpy pillows have been photographed at modern volcanic centres in the Pacific Ocean, often in quite deep water.

Thus the primary sediment is a grand mixture of just about everything that can resist weathering and be washed off the continent, everything that can form by weathering and all the things that organisms secrete. It is wet both because of chemically bound water and because of a high porosity. It is reactive, because it contains so many fine particles and even amorphous materials.

As this material is covered and buried the first process to occur involves the reduction in porosity. At the surface pore volume may be as large as 40 per cent but by the time burial reaches 2 km this is reduced to 1–2 per cent. At 5 km depth, it is vanishingly small. Porosity will be in part removed by purely mechanical processes and in part by more soluble materials dissolving at site of stress concentration and reprecipitating in stress shadows. By the time the rock reaches this 5 km burial, most of the water will be bound in hydrated minerals. Many of the main sedimentary minerals will still be rather stable but some more reactive materials may have been reorganized.

As the sediments sink they will also be heated by the normal heat flow coming from the interior of the earth. Unless the rate of accumulation is catastrophically fast they will reach thermal equilibrium almost as fast as they sink. Heat flow and conductivity measurements show that temperatures will rise by something

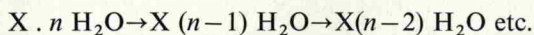
Phase changes in the earth's crust

like 10–30°/km. By the time 5 km burial is achieved, temperatures will be of the order of 100°C. A few reactions that might be expected to proceed even under these mild conditions would include:

- metastable aragonite → calcite
- amorphous silica → fine quartz
- amorphous clay materials → crystalline clays and chlorites
- very fine crystals → larger crystals

By the time these processes have occurred, the muddy sediment has become a rock.

Even at quite moderate temperatures some of the hydrated minerals may proceed to dehydrate. Normally these dehydration reactions can be envisaged to proceed in steps:



With most familiar chemical hydrates these steps are distinct and lead to a regular pattern of vapour-pressure curves (Fig. 3). But when extensive solid

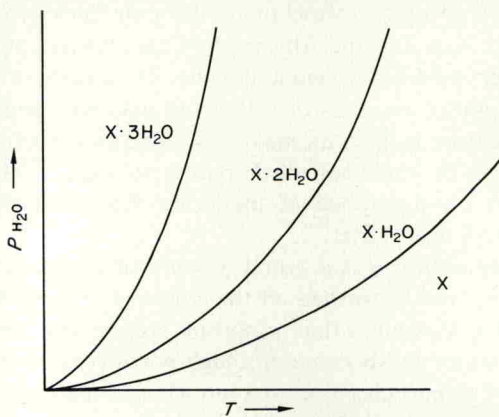


Fig. 3. The normal form of vapour pressure curves for a series of hydrates at low pressures.

solutions are involved as with clay minerals and chlorites, one may expect a more or less continuous dehydration reaction.

If porosity is large, water may flow out via a continuous pore system. If this occurs, the water pressure will be about that corresponding to a water column of appropriate height. The pressure on the solid phases will be greater for these must bear the load of sediment. Thus to a first approximation, in the upper levels, $P_{\text{H}_2\text{O}} \approx \frac{1}{3} P_{\text{rock}}$.

As sinking continues, porosity and permeability begin to decline to very small values. Heating and water evolution continue but the released fluid has a more difficult task fighting its way to the surface. Measurements in deep bores have