tion of 320 ppm (*6*) would be 7.77 in the Willamette River and 8.13 in the Columbia River (Fig. 2). Our observed pH values are over 0.3 unit less than the equilibrium pH.

The CO_2 pressure we monitored in the river is much higher than that in the atmosphere. This is contrary to the simple supposition that any flowing water would equilibrate rapidly with the atmosphere. Furthermore, any appreciable concentration of carbonic anhydrase in water also would facilitate rapid equilibration (*7*). The oversaturation we observed must be maintained by the combined net effect of the high concentration of CO_2 in source water such as soil water, biochemical oxidation *in situ*, and the rate of escape of CO_2 from the river to the atmosphere.

This study demonstrates that it is possible to calculate within a precision of ± 5 percent the CO_2 pressure in river water by measurements of pH, total CO_2, and temperature. Confining the method to these measurements involves less expensive equipment than the infrared analyzer and would be adequate for many purposes.

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Graywacke Matrix Minerals: Hydrothermal Reactions with Columbia River Sediments

Abstract. *Experiments with sands chemically similar to graywackes produced "matrix" minerals at 250°C and a water pressure of 1 kilobar. Starting materials were moderately well sorted sands containing abundant volcanic rock fragments and no detectable clay minerals. The results support the concept that graywacke matrix may form diagenetically by hydration and recrystallization of unstable clasts. Matrix need not be a recrystallized detrial fine fraction. Texture, therefore, is not a reliable criterion for sandstone classification. For graywackes, chemical composition may be more significant.*

Whetten (*1*) demonstrated the similarity in mineral and chemical composition between sediments from the bed of the Columbia River and typical graywackes, in spite of the fact that Columbia River sediments are, in general, much better sorted for size than graywackes. He concluded that "sediments from the Columbia River could be used in an attempt to produce a graywacke in the laboratory" and thereby to test Cummins' hypothesis (*2*) that graywacke texture is postdepositional in origin, occurring when chemically unstable grains are hydrated and recrystallized to form matrix during weathering, deep burial, or low-grade metaphorism. Accordingly, we now report a series of hydrothermal experiments.

We used three typical samples of Columbia River sediments as starting materials to test the feasibility of forming graywacke matrix minerals in hydrous environments at elevated temperatures and pressures. The results of the experiments indicate that phyllosilicates and zeolites (matrix minerals) form readily under conditions equivalent to burial at 3 to 4 km and geothermal gradients of 60 to 80°C/km.

The original samples are moderately well sorted sands composed of quartz, labradorite, clinopyroxene, orthopyroxene, hornblende, biotite, muscovite, opaques, volcanic glass, and volcanic clasts of basaltic and andesitic compositions. Clay minerals are present only in small quantities; they are not detectable by x-ray diffraction unless they are concentrated from large volumes of sediment. Montmorillonite is the most abundant clay mineral in sediments from the section of the river where the samples were obtained (*3*). Chemical analyses of the samples and a comparison wtih typical eugeosynclinal graywackes of the Pacific rim are presented in Table 1.

The sediment samples were ground to −200 mesh in an alumina mortar. Charges were prepared by placing 0.100 g of ground sample plus 0.10 ml of fluid (either double-distilled water or an artificial seawater solution) in annealed silver tubes. The tubes were crimped flat to remove most of the air and were welded. The sealed tubes were heated externally in cold-seal stainless steel rod bombs by resistance furnaces. Both internal bomb pressure and external bomb temperature were monitored during the experiments; temperature variation was less than ± 12°C, and pressure variation was less than ± 300 pounds per square inch (approximately ± 20 bars). Charges were weighed before and after the experiments to check for possible gain or loss of material. Experiments were made at 1 kb P_{H_2O} and at temperatures of 150°, 250°, and 300°C. The experiments lasted from 21 to 60 days.

Reaction products were analyzed by comparison of x-ray diffraction patterns of approximately equal weights of heated and original samples mounted on ceramic tile by the suction technique (*4*). Clay mineral groups were identified by glycolation and heating tests. Clinoptilolite was distinguished from heulandite by Mumpton's method (*5*). The tentative identification of riebeckite was based on comparison of reaction products with three distinctive peaks [(110), (040), (310)] given in the American Society for Testing and Materials diffraction data. Curiously, the (110) peak disappeared when the sample was heated to 550°C in the open atmosphere during a test for clay minerals. Plagioclase compositions were determined by spacings of (131) and $(1\bar{3}1)$ diffractogram peaks (*6*). At least some of the glass in the original sample was retained in products of the experiment and was identified optically. Minerals identified as synthesized products were not detected in the original sediment. Mafic minerals, plagioclase, and volcanic rock fragments (including glass) were probably important species in reactions producing the new minerals. Reaction products are listed in Table 2.

Table 1. Chemical analyses of graywackes. Samples: 1, Columbia River sample CC43 (wet chemical analysis); 2, Columbia River sample CC72 (x-ray fluorescence); 3, Columbia River sample CC148 (wet chemical analysis); 4, average of 68 Columbia River sediment samples (*9*) (by x-ray fluorescence); 5, average Franciscan Formation graywacke (*10*); 6, average New Zealand graywacke (*11*).

Constituent	1	2	3	4	5	6
SiO_2	67.53	67.3	63.22	66.5	67.5	69.3
TiO_2	0.71	0.9	0.85	0.8	0.5	0.5
Al_2O_3	14.10	13.4	16.13	13.9	13.5	14.3
Fe_2O_3	2.46	7.4	2.91	4.7	1.2	1.0
FeO	1.83	*	2.52	*	3.0	2.6
MnO	0.07	0.1	0.10	0.1	0.1	0.1
MgO	1.67	3.5	2.67	2.0	2.2	1.4
CaO	3.36	3.5	5.03	3.4	2.4	1.9
Na_2O	3.08	3.5	3.82	2.9	3.6	3.6
K_2O	2.30	2.1	1.60	2.1	1.7	2.6
H_2O^+	1.03		0.70		2.5	2.0
H_2O^-	1.70		0.20		0.4	0.3
P_2O_5	0.18		0.29		0.1	0.2
CO_2					0.8	0.1

* Total iron expressed Fe_2O_3.

Table 2. Summary of hydrothermal experimental results at 1 kb P_{H_2O}. DW, distilled water; ASW, artificial seawater; Chl, chlorite; Mnt, montmorillonite; Cpt, clinoptilolite; Heu, heulandite; Rie, riebeckite; (?), quantities too small for certain identification.

Experiment	Duration (days)	Temperature (°C)	Fluid phase	Synthesized products		
				CC43	CC72	CC148
1	30	300	DW	Chl Mnt Cpt	Mnt	Mnt
2	21	150	ASW			
3	29	250	ASW	Mnt Chl	Mnt	Mnt (?)
4	28	150	ASW			
5	60	250	DW	Mnt	Mnt Heu	
6	60	250	DW	Mnt (?)	Chl (?)	
7	60	300	DW	Mnt	Mnt Cpt Rie	Chl Mnt

The most abundant production of new minerals occurred in experiments 1 and 7. Decrease in the diffractrogram peaks heights of quartz and orthopyroxene in experiment 7 are interpreted as an indication of destruction of these minerals as the new assemblage developed; plagioclase of this synthesized assemblage is more calcic than that of the original material. The peak changes observed are interpreted as due to the modification of these phases as riebeckite developed. The increase in anorthite content of plagioclase suggests removal of albite components to form the amphibole. In experiments 1 and 5, peak changes suggested an increase in quartz and albitic plagioclase, the expected products in low-temperature reactions in sediments of this composition. The low temperatures and short durations of the experiments probably slowed reaction rates. Generally, the longest runs produced the most abundant new minerals for any given temperature. The role of volcanic glass in these reactions cannot be determined quantitatively, but in terms of the reaction kinetics we assume that it was important.

Interpretation of the experimental results appears to confirm the suggestion that the graywacke "matrix" mineralogy may be produced by hydration and recrystallization of detrital grains. However, the fluid phase during the experimental runs was oxidizing and probably had a moderately high *p*H. These conditions, especially the oxygen partial pressure, probably are not typical of graywacke environments where reducing conditions may prevail.

The highest temperature used (300°C) produced the most abundant products, but this temperature probably exceeds the conditions associated with alteration of graywackes. It is apparent, however, that matrix minerals were developed at 250°C; in natural environments, where time is not a limiting factor and where shearing may play a role in promoting reaction rates, it is assumed that the same assemblages form at still lower temperatures.

The apparent formation of riebeckite in experiment 7 is attributed to the fluid composition described above plus the relatively high content of iron and the high ratio of Na_2O to K_2O in the sample. In a reducing environment it is likely that riebeckite would be supplanted by phases such as chlorite and albite. To our knowledge, riebeckite has not been reported as a graywacke matrix mineral although it is found as a diagenetic mineral in environments with a high *p*H (*7*). Our conclusions and inferences follow.

1) We have synthesized minerals that typically occur in the matrix of graywacke-type sedimentary rocks. In graywackes, these minerals are commonly interpreted either as primary detrital minerals or as recrystallized fines with little or no change in mineral composition.

2) Modern sands having the bimodal character of graywackes are not common and are rare in the marine realm (*8*), which, judging from the lithologic character of ancient graywackes, should be one of the most likely sites of deposition of such sediments. Sands having the chemical composition of ancient graywackes do occur as modern sediments (Table 1). In particular, they seem to be typical of areas of rapid sedimentation, such as those near the ocean margins.

3) We have not observed graywacke texture in our run products because of the limitations of our experiments, but we believe it is reasonable to assume that the synthesized products have the same textural relation to surviving grains as graywacke matrix.

4) Our results support Cummins' assertion (*2*) that matrix minerals in graywackes may result from postdepositional alteration of geochemically un-

stable detrital sand grains. We do not imply that all graywackes are formed in this manner; some may have a primary detrital matrix. However, the importance of diagenesis should not be overlooked as a process that can bring about profound changes in mineralogy and texture, especially in sediment derived from a geochemically immature source area such as the drainage basin of the Columbia River.

5) Several commonly used sandstone classification schemes are based in large part on the amount of matrix present, which is tacitly assumed to be a genetic property related to sorting by the transporting medium. The usefulness of this property is open to serious question unless one can prove that the matrix is of primary depositional origin.

6) It is apparent that eugeosynclinal graywackes encompass a restricted range of chemical compositions equivalent to hydrated (and in many cases oxidized) andesites and dacites. The chemical similarity between andesite-dacite and graywackes is perhaps easily understood in terms of the general petrogenic association of graywackes and intermediate composition volcanic rocks in zones of active tectonism. We suggest that consideration be given to using chemical composition and mineral content as major parameters in classifications of clastic rocks. This would avoid ambiguities arising from reliance on textural features that may be the result of extensive postdepositional modification.

7) Knowledge of the compositions of the fluid phase is critical to understanding the stability relations of the synthesized minerals.

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Mawson "Tillite" in Antarctica: Preliminary Report of a Volcanic Deposit of Jurassic Age

Abstract. *Reexamination of the Mawson "Tillite" (Jurassic) of Antarctica indicates that the deposit is of volcanic origin and consists largely of both primary and reworked volcanic materials. No evidence diagnostic of a glacial origin was found.*

Gunn and Warren (*1*) in their report on the geology of south Victoria Land, East Antarctica, introduced the name "Mawson Tillite" for a poorly sorted rock supposed to be the product of glacial deposition. (The term tillite will be retained in this report although our work indicates that the rock is not a tillite.) This unit, which crops out on nunataks for over 100 km along the western side of the Transantarctic Mountains, was assigned to the Jurassic System (Fig. 1). The suggested existence of such an extensive glacial deposit of Jurassic age conflicts with some precontinental drift reconstructions of continents of the Southern Hemisphere. For example, the reconstructions of King (*2*) and Runcorn (*3*) place Victoria Land much closer (approximately 40° south latitude) to the Equator during the Jurassic than it is at present. Moreover, glacial deposits of this age have not been reported from any other Southern Hemisphere continent.

A later expedition to south Victoria Land concluded tentatively that the main mass of the tillite (on Allan Nunatak) is a subaerial explosion breccia and volcanic mudflow, although the evidence for such an origin was admittedly only suggestive (*4*). Ballance *et al.* (*4*) also concluded that the origin of the tillite at Carapace Nunatak (Fig. 1) was different from that of the main mass of tillite. It is at Carapace that Jurassic fossils date the tillite (*1, 5*) and, therefore, the age of the main mass of tillite was opened to question.

Our own work centered on three nunataks—Allan, Carapace, and Battlements (Fig. 1). In this preliminary report, the geology of each will be considered in turn.

At Allan Nunatak, Gunn and Warren (*1*) reported over 1300 feet (396 m) of Mawson Tillite resting with disconformity on Permian coal measures assigned to the Beacon group. The Mawson at Allan Nunatak consists of two distinct lithologies. A lower unit, zero to several meters thick, is a mixture of distorted and granulated rocks of the Permian Beacon sandstone and shale, plus fragments of the basalt that intrude the Beacon. The upper unit, which is at least 300 m thick, is distinctly different from the lower one and is a poorly sorted rock partially derived from granulated Beacon rocks but largely from basaltic volcanic material.

Several features indicate that the upper unit is a volcanic mudflow and not a tillite. First, volcanic fragments in the rock are distended and envelop matrix material in a manner that could have been accomplished only while the fragments were hot and mobile. Second, the unit contains abundant, highly indurated, probabably "baked" fragments of Beacon sandstone. Third, thick graded beds on the scale of several tens of meters are present. This latter feature is characteristic of volcanic mudflows (*6*) but is not found in tills (with the possible exception of tills deposited from ice shelves or floating glaciers.) Often the tops of these thick graded beds appear to be worked by water (Fig. 2). The association of these deposits with contemporary igneous activity is further seen by the presence of basalt dikes in the Mawson that have been strung out as if intruded prior to final rest and consolidation of the moving Mawson mass (*4*). A concluding argument against a glacial origin is the apparent lack of striated, grooved, and soled clasts that are almost universally present in till.

The lower unit of the Mawson is gradational from the underlying undistorted Beacon sandstone, through distorted Beacon, to fragments of Beacon in a granulated Beacon matrix. The Beacon sandstone has been distorted, fragmented, and strung out by mass