THE PETROLOGY, STRATIGRAPHY AND BASIN HISTORY OF THE MONTESANO FORMATION, SOUTHWESTERN WASHINGTON AND SOUTHERN OLYMPIC PENINSULA

(Chapter 3: Diagenesis of the Montesano Formation)

A Thesis Presented to the Faculty of

Western Washington University

In Partial Fulfillment of the Requirements for the Degree

Master of Science

Phillip Kenneth Bigelow

May, 1987

DIAGENESIS OF THE MONTESANO FORMATION

By Phillip Kenneth Bigelow

All of the stratigraphic sections were studied for diagenetic alteration. Laboratory techniques involved the analysis of thin sections, X-ray diffraction studies, including the Green-Kelly test for beidellite (as described by Green-Kelly, 1955), and scanning electron microscopy.

DIAGENETIC FACIES

The Montesano Formation has experienced a low-temperature and low-pressure zeolitic diagenesis in the clinoptilolite-smectite facies in a marine environment. The diagenesis is regional in extent and crosses all lithofacies except for the top 138 meters of the Canyon River section and the uppermost middle and upper members of the Pack Sack section. Using the diagenetic tables from Hoffman and Hower (1979) as a guide, the temperatures involved in the diagenesis of Montesano sandstone did not exceed 50º-60º C and they may have been lower. The rocks that lack diagenetic minerals are strata that were deposited in the nonmarine(?) facies of the Formation and remain unaltered.

MARINE FACIES: DIAGENETIC PROCESSES AND MINERALS (PARAGENESIS)

X-ray diffraction analysis of all orientated clay samples showed a very sharp high-intensity (001) peak with a d-spacing of 14.73 angstroms. This d-spacing indicates a well-crystallized clay with either Ca^{++} , Mg^{++} or both cations filling the interlayer region of the basal spacing of the smectite. The Green-Kelly test (Li^{+} substitution) showed that the majority of the smectite is montmorillonite, with a small amount of beidellite.

The clinoptilolite and Mg-Ca smectite cements are derived entirely from the alteration or the dissolution of volcanic glass in the Formation. Glass shards and larger vitric and hyalopilitic clasts have been pseudomorphed by clinoptilolite. In microlitic clasts, the interstitial glass has been altered, while the feldspar microphenocrysts and microlites remain unaltered. Dissolution of volcanic glass and pseudomorphic replacement of volcanic glass often occur together; however, dissolution of volcanic glass was a much more frequent process. Dissolution has effectively removed 9% of all volcanic lithic grains, and, more specifically, has removed 50% to 83% of the dominantly vitric grains in the marine facies of the Formation. Unaltered (fresh) glass is uncommon in the deeper marine facies and is more common in shallower, near-shore facies (e.g., the Aberdeen section).

The abundance of pseudomorphed glass shards in the marine facies is variable. Some outcrops contain white patches of altered glass that resemble finely-ground shells mixed with a dark gray sandstone. When examined microscopically, most pseudomorphed glass shards appear angular and extremely delicate, suggestive of air-fall deposition. The shards range in size from 0.16 mm to 0.90 mm.

Relative age relationships were established for most of the diagenetic features in the Formation. These relationships were identified by the sequence of cavity fillings, by inclusions of one mineral in another, by replacement, and by intergrowth of two minerals. The order of diagenesis in the Montesano Formation follows (see also Figure 38).

1) Bioturbation.

2) The beginning of the decomposition of organic matter, with associated authigenesis of pyrite. Pyrite is the earliest diagenetic mineral, although the mineral formed in greater amounts after clinoptilolite cement. Pyrite continued to form in lesser amounts after late-stage calcite cement.

3) Dissolution of volcanic glass.

4) Precipitation of magnesium-calcium (Ca^{++} - Mg^{++}) smectite fringing cement (a montmorillonite-beidellite mixture) in the pore spaces.

5) Pseudomorphic precipitation of clinoptilolite within the volcanic glass voids.

6) An early stage of fringing sparry or drusy calcite cement or a stage of formation of botryoidal masses of fibrous calcite cement. Early stages of calcite cementation are not present in all calcite-cemented samples.

```
                         |---------------------------Increasing compaction-------------------------------->|

1) Bioturbation     |--------|

2) Pyrite authogenesis   |----------------          ------                                                ----------|

3) Dissolution of volc. glass         |-------|

4) Montmorillonite cement                      |----------------|

5) Zeolite pseudomorphism of volcanic glass                     |--------|

?) Aragonite             |. . . . . . . . . . . . . . . . ? . . . . . . . . . . . . . . . . . . |

        6) Early-stage calcite                                  |----------------|

            7) Clinoptilolite fringing cement                                     |-------|

                8) Late-stage calcite                                                    |------|

                    9) Gypsum                                                                   |-------
```

Figure 38. Relative order of diagenesis in the Montesano Formation. Time decreases toward the right. The graph shows all phases of alteration in a marine environment. Not all diagenetic minerals or processes occur in all samples. Aragonite's dotted line signifies an uncertain position in the diagenetic order.

7) Clinoptilolite fringing cement.

8) A late stage sparry calcite cement that fills the remainder of the pore space (in concretions).

9) The formation of gypsum. Holocene mineralization.

Diagenetic aragonite occurs locally in the Formation. Aragonite formed before the late-stage calcite cement, but its position in the diagenetic order is not otherwise known.

Alteration of Organic Material (Stage 2 Through Stage 8)

In carbonate concretions, wood fragments occur in various stages of early alteration (having a light yellow, red or dark reddish-brown resinous color). A well-preserved cell structure is usually present. In general, completely carbonized wood is uncommon in concretions. Diagenetic stages 6 and 8 halted further carbonization of the wood and preserved the cell structure. The light coloration of the woody material indicates that the degree of thermal maturation was low prior to calcite cementation. Beds that lack carbonate cement contain completely carbonized wood (coal).

Pyrite (Stage 2 Past Stage 8: Discontinuous)

Pyrite is generally volumetrically sparse. The mineral is more common in sediments rich in organic matter. Pyrite occurs as spherical clusters of crystals (framboids) 0.075 mm to 0.100 mm in diameter. Framboids range down to 3 microns. Single octahedral to cubic crystals are commonly 0.01 mm (all measurements were made with scanning electron microscopy). The mineral occurs as an authigenic geopetal filling in foraminiferal tests, as scattered authigenic clusters in mudstone, and as an incomplete pore cement.

Pyrite in foraminiferal tests is geopetal. In burrowed sediment, pyrite invariably occupies the bottoms of the tests' cavities, suggesting that the growth of the pyrite was completed after bioturbation. Pyrite growth probably started after burial.

Some volcanic lithic grains have a thin rim of pyrite replacing the inner margin of the clasts. The grains are subsequently externally coated with smectite and clinoptilolite fringing cements (stages 4 and 7). Pyrite continued to form in greater amounts after stage 7 (clinoptilolite fringing cement). A substantial decrease in growth occurred after stage 8. Pyrite growth ceased before stage 9.

Aragonite (Before Stage 6)

Slender, radiating aggregates of columnar to acicular aragonite occur in fossil wood in calcite-cemented concretions. The mineral was confirmed by X-ray diffraction. The aragonite formed sometime before the calcite, but the exact position of the mineral in the diagenetic order is unknown.

Dissolution of Volcanic Glass (Stage 3)

Three relationships indicate that dissolution of volcanic glass occured prior to zeolite pseudomorphism:

1) The lower and middle marine members of the Canyon River section are depleted in total volcanic lithic grains compared to the top of the upper member. The latter unit is nonmarine and experienced little diagenesis (see Diagenesis: Nonmarine Facies).

2) Delicately preserved voids (molds) of dissolved glass shards occur in what was a tuffaceous muddy siltstone bed in the marine lower member of the Canyon River section. Zeolite pseudomorphic replacement did not coincide with dissolution.

3) In pseudomorphed glass shards, a central void is often present.

The dissolution of volcanic glass occupies a well-defined position in the diagenetic order. Early-stage pyrite occurs in the surrounding matrix but is absent in pseudomorphed glass shards. Pseudomorphed glass is sometimes internally rimmed by smectite. Clinoptilolite fills the remainder of the void.

Mg-Ca Smectite (Montmorillanite-Beidellite Mixture) (Stage 4)

Diagenetic Ca-Mg montmorillonite-beidellite was confirmed by X-ray diffraction analysis of matrix-free sandstone samples that contain clay cement. The diffraction patterns indicate that the clay is well-crystallized, and the Green-Kelly Test (Li^+ saturation) for beidellite was positive. Lithium cation substitution plus glycerol treatment also showed that montmorillonite is present. The smectite occurs as a fringing cement in pore spaces (Figure 39), and is fringed with clinoptilolite pore cement (stage 7). In facies that are transitional between marine and nonmarine environments, the montmorillonite-beidellite can occur alone as a fringing cement in pore spaces.

Smectite crystallization is partly contemporaneous with, but mainly postdates, early-stage pyrite authigenesis. The clay generally coats early-stage pyrite.

Clinoptilolite as a Pseudomorphic Replacement of Volcanic Glass (Stage 5)

Clinoptilolite was identified by X-ray diffraction. Clinoptilolite is distinguished from the calcium-pure end-member heulandite by a characteristically strong peak at 8.99 angstroms and a less intense peak at 3.96 angstroms (Chen, 1977). The deep red stain imparted to the zeolite by the barium-amaranth method indicates that the clinoptilolite in the Montesano Formation contains a significant amount of calcium.

Zeolite-replaced grains are volumetrically less abundant than zeolite cement. Two types of pseudomorphism occur in the Formation: 1) in-filling (cementation) of a mold (refer to stage 3) and, less commonly, 2) direct replacement. Direct replacement (pseudomorphism that lacks an

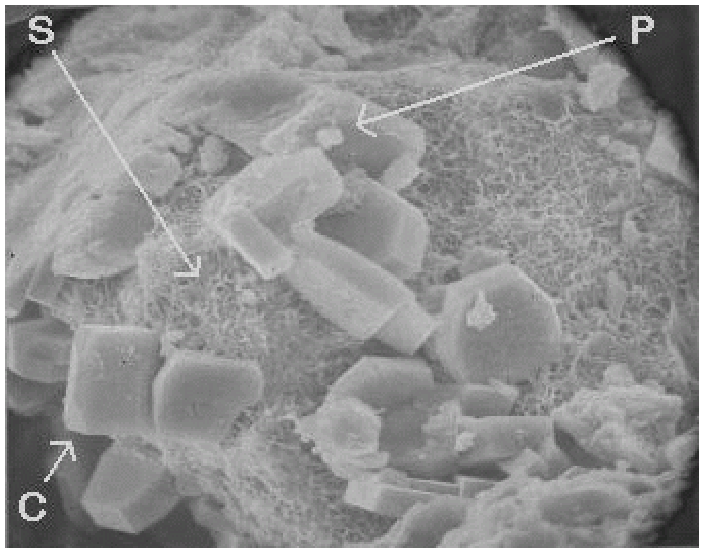

Figure 39. Scanning electron photomicrograph of stage 4 diagenetic smectite cement (S; finely crystallized platy aggregates), overgrown by stage 7 clinoptilolite cement (C; large euhedral crystals). Both cements are coating a rounded framework grain. The small irregular to spheroidal masses are post-stage 7 framboidal pyrite (P). Montesano Formation sample A-1-1. Field of view is 0.17 × 0.13 mm.

intermediate step involving dissolution) is inferred to have taken place in sandstone lacking a mud matrix and with a high porosity. Molds of dissolved glass cannot exist without a mud matrix. The pseudomorphed glass is externally rimmed by stage 6 sparry, drusy or fibrous calcite, or by stage 7 clinoptilolite fringing cement. A similar occurrence of replacement by mold-filling and by direct replacement of volcanic glass by clinoptilolite was reported from the John Day Formation by Hay (1963).

<u>Clinoptilolite Fringing Cement (Stage 7)</u>

Small, equant orthorhombic crystals of clinoptilolite fringing cement are the most common form of the zeolite in the Formation (Figure 40). The crystals are stubby and are much smaller than the zeolites that occur in replaced volcanic glass. The crystals commonly range from 0.011 mm to 0.037 mm and average 0.026 mm.

Smectite fringing cement (Stage 4; Figure 39) and early-stage calcite fringing cement (stage 6) invariably precede clinoptilolite fringing cement. Late-stage pyrite formed after the zeolite.

<u>Calcite Cement (Stages 6 and 8)</u>

Calcite is volumetrically the most abundant cement in concretions. In medium-grained, well sorted sandstone, the mineral occupies an average of 66% of the total pore space. The remaining 34% of the pore space is occupied by zeolites, clay and pyrite.

Early-stage calcite (stage 6) is most commonly a thin sparry or drusy fringing cement. Pore-filling fibrous calcite is also observed in concretions but is much less common. The calcite often discontinuously rims the pore. Stage 7 clinoptilolite fringing cement can grow on both early-stage calcite and on a framework grain within the same pore space.

Rarely, the growth of stage 6 fibrous calcite filled the pore and formed botryoidal concretions. A layer of pyrite (averaging

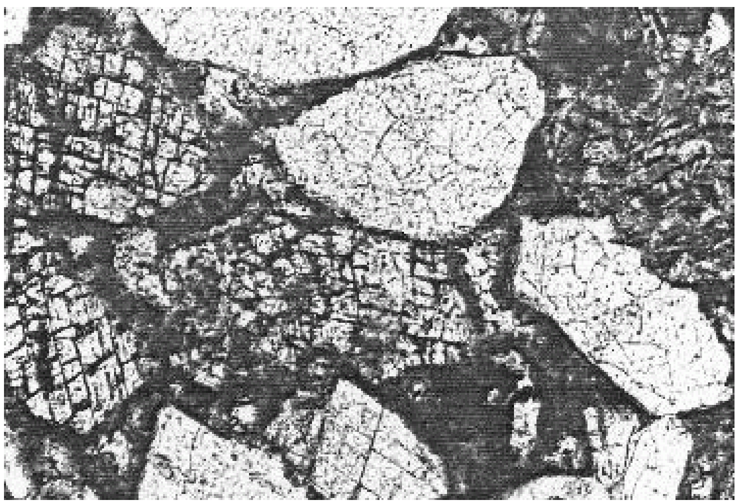

Figure 40. Photomicrograph of potassium feldspar grains (stained yellow), quartz grains (clear) and volcanic grain (right) fringed with stage 7 clinoptilolite cement (deep red stain). Remnant porosity (clear) exists in the center of the pores. Montesano Formation sample A-1-6. Field of view is 0.85 × 0.58 mm. Plane polarized light. Stained.

0.037 mm thick) outlines the terminus of growth of the botryoidal calcite, and appears to have been pushed ahead of the calcite growth surface. Subsequently, stage 7 clinoptilolite fringing cement, a later stage of framboidal pyrite, and stage 8 sparry calcite cemented the botryoidal masses together.

Late-stage calcite cement is commonly a mosaic of coarse spar. Microspar is much less common. Poikilitic calcite is rare, and, where present, coexists with mosaic spar. Late-stage calcite postdates all other diagenetic minerals except small amounts of late-stage pyrite and gypsum. A few late-stage calcite concretions are fractured and veined with pyrite and calcite that is texturally similar to stage 8 calcite.

Replacement of Framework Grains by Calcite (Concurrent with Stage 6 or Stage 8)

If calcite-cemented samples are compared to samples without calcite cement, Q-F-L and Qm-F-Lt modes show a depletion in categories (L) and (Lt) of 11% and 10%, respectively. Hypersthene, hornblende and, rarely, quartz exhibit minor partial replacement along the edges of grains.

Compaction and Changes in Porosity (Stage 2 Past Stage 8)

Compaction of the sediment occured before and after the growth of the concretions. An average reduction of 11% in total porosity occured as a result of further compaction of the surrounding sediment after the growth of the concretions. The average total porosity preserved in concretions is 27%, and the average total porosity in non-carbonate-cemented samples is 16% (total porosity = all pore cement + void space, if present). All analyzed samples are well- to moderately-sorted and are medium-grained. In adjacent beds in the Aberdeen section, a 12% reduction in porosity occured after the growth of concretions, which is consistent with the average value for the whole Formation.

Remnant porosity (voidal porosity) averages 5.7% in non-carbonate-cemented sandstone beds, and averaged 17.3% prior to calcite cementation in concretions.

<u>Gypsum (Stage 9)</u>

Small radiating aggregates of acicular gypsum (identified by X-ray diffraction) occur in some of the samples. The aggregates average 0.50 mm in diameter. The mineral is common in sandstone-mudstone interlayers, where it collects in partings between the two units. The gypsum also occurs as a crust on carbonized wood fragments. The mineral is not found in concretions, and it is free of other overgrowths. The gypsum is therefore believed to be a very late-stage (Holocene) mineral. Deer and others (1966) note that gypsum can form from weathering of calcium-rich minerals caused by percolating meteoric waters.

UNALTERED VOLCANIC GLASS FACIES

A dominantly unaltered volcanic glass facies is assigned to the upper 138 meters of the Canyon River stratigraphic section (Figure 16; Appendix T) and to the top of the middle and the upper members of the Pack Sack section on the basis of the following relationships: 1) the occurrence of unaltered volcanic glass shards; 2) the absence or scarcity of pyrite; 3) the absence of smectite and clinoptilolite cement (except in a short transitional diagenetic facies about 430 meters above the base of the Canyon River section, where smectite can occur alone); and 4) the absence or extreme rarity of calcite cement.

REFERENCES CITED

Chen,P. 1977. Table of key lines in X-ray powder diffraction patterns of minerals and clays and associated rocks. Indiana Department of Natural Resources Geological Survey Occasional Paper 21, 67 p.

Deer, W. A., Howie, R. A., and Zussman, J. 1966. An Introduction to the Rock-forming Minerals. Longman House Press, Essex, United Kingdom, 528 p.

Fowler, G. A. 1965. The stratigraphy, foraminifera, and paleoecology of the Montesano Formation, Grays Harbor County, Washington. Unpublished PhD thesis, University of Southern California, Los Angeles, 355 p.

Green-Kelly, R. 1955. Dehydration of the montmorillonite minerals. Mineralogic Magazine 30: 604-615.

Hay, R. L. 1963. Stratigraphy and zeolitic diagensis of the John Day Formation of Oregon. University of California Publications in the Geological Sciences 42, no. 5, pp. 199-262.

Hoffman, J., and Hower, J. 1979. Clay mineral assemblages as low grade metamorphic geothermometers - application to the thrust faulted disturbed belt of Montana, U. S. A., *in* Scholle, P. A., and Schulugar, P. R., eds., Aspects of Diagenesis. Society of Economic Paleontologists and Mineralogists Special Publication 26: 55-79.

Appendix T

Stratigraphically-Highest Occurrences of Various Facies In The Montesano Fm: Canyon River Section