KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORT ND-11

FLORENA SHALE

by

J. Imbrie

Kansas Geological Survey
1930 Constant Avenue
University of Kansas
Lawrence, KS 66047-3726

Florena Shale
By John Imbrie

Chert

Dolomite

Hematite

Illite

Montmorillonite

Pyrite

Sericite

Illite and montmorillonite must be treated as separate minerals, although this does injustice to the actual mineralogical mode of occurrence as determined by X-ray.

Three minerals had to be assumed in order to exhaust the stated chemical analyses completely: gypsum, to use up the SO_3; spene, for TiO_2; and sepiolite, to take care of the rare instances with the ratio of MgO to K_2O exceeds a critical value. In no case did any of these three hypothetical minerals exceed a trace amount. Chemical compositions of all minerals used in computation are given in Table 3.

It will be apparent to the reader that the precise calculation system embodied in the calculation form below will not be generally applicable. The mineralogy of each case must be examined and treated appropriately. For example, the presence of chlorite or kaolinite (nor present in the Florena samples under discussion here) would entail certain modifications of the form.

<u>Explanation of the form</u>. Step I: The first step in using the form (Figure 2) to enter in the appropriate boxes on the left hand side weight percentages of the various oxides derived by chemi-

cal analysis. Each of these is then converted into a molecular proportion by dividing the oxide weight by the molecular weight, and the result entered in the appropriate box. It is usually desirable to carry five decimal places in calculation; hence, for simplicity, this number of places is assumed throughout and decimal points and zeros are eliminated. An entry of 99, for example, represents an actual molecular proportion of .00099.

Each blank box on the calculation form having some special significance is designated by a symbol, usually a capital letter, so that this quantity may be conveniently and unambiguously referred to again. Thus *A* stands for the molecular proportion of SO_3, *T* the molecular proportion of Na_2O and so on. In some cases a symbol stands for a quantity needed for more complex types of calculation.

Step II: Calculate minor constituents by multiplying molecular proportions of the key oxides (*A*, *D*, *B*, *T*, and *C*) by the appropriate molecular weight.

Step III: Calculate carbonates as follows: From the molecular proportions of CO_2 subtract the total number of molecules of CaO remaining after allowing for CaO used in gypsum, apatite, and sphene (total CaO - *A* - 3*B*- *C*). The balance (*E*) represents the amount of dolomite necessary to use up all of the CO_2. By subtracting *E* from the available CaO the molecular proportion of calcite is determined. When the total MgO and CaO are insufficient to use up CO_2 (*F* 0), ferrodolomite is calculated as indicated.

Step V: In calculating clays, two first order alternatives are possible depending on the relative proportions of K_2O and MgO.

If the ratio s H/2 F equals of exceeds 1 (alternative iiA) all of the MgO is computed as illite, and the balance of the K_2O not used as illite is computed as sericite. If 3 H/2 F is less than 3/2, two second order alternatives (iiB and iiC) are possible depending on the relative amount of Fe_2O_3 and K_2O. If Fe_2O_3 - $4K_2O$ + Al_2O_3 is greater than zero (G - delta 70) the K_2O is calculated as illite, and the remaining MgO is sepiolite (Alternative iiB). If (G - delta O) the remaining oxides with the exception of silica are computed as sericite, iron rich sericte, montmorillonite, and sepiolite, (Alternative ii C).

Two third order alternatives are now possible (iiB_1 and iiB_2) depending on the relative amounts of K_2O and Al_2O_3 (8N - K). If K_2O is in excess of the designated proportion, illite and hematite are calculated; if K_2O is less than the designated proportion, illite and montmorillonite are calculated.

In calculating weight percentages of illite and montmorillonite which contain varying amounts of Fe_2O_3 and Al_2O_3, provision has been made for determining the appropriate molecular weight.

Step VI: SiO_2 unused up to this point is now totaled and calculated as chert.

Step VII: Blank spaces are provided on the form for entering totals of minor constituents, carbonates, clays and chert. For purposes of the Florena study it was desirable to represent each sample on a triangular diagram having as end members calcite, dolomite (including ankerite), and total clay. Blank spaces to facilitate this calculation are also provided.

Step VIII: Compute the total bound water (H_2O+) as indicated in item V.

Step IX: Two different checks are built into the form. The first (item vii) checks the accuracy of the arithmetical work by ignoring the figure for loss on ignition representing SO_2, H_2O-, H_2O+, and organic matter. A dry total calculated by adding the stated weight percentages of oxides from SO_3 through SiO_2 is compared with a dry total calculated by summing the calculated weight percentages of minerals (Subtotal 2), from which the calculated bound water is subtracted. It is also necessary to take into account a discrepancy introduced by the fact that iron used in the calculation of ankerite and pyrite is actually ferrous iron. This is done by adding the factors 8Y and 24D.

Step X. Finally, the original stated analysis including loss on ignition may be compared with the computed total including bound water. This is done (items i and vii) by computing two wet totals. Wet $total_1$ is derived as follows: from the figure given for loss on ignition 140° (H_2O+ + SO_2 + organic matter) subtract the weight lost by evolution of SO_2. This gives a figure for the total of H_2O+ and the remaining oxides gives $subtotal_1$. This must now be corrected for oxygen used in forming ankerite and SO_2. Wet $total_1$ is now compared with wet $total_2$ determined by adding $subtotal_2$ (the sum of computed minerals), the figure for computed organic matter, and the observed H_2O-. The "wet total check" is sensitive not only to inaccuracies of laboratory procedure in determining the various losses on ignition but to incorrect assumptions as to the state of hydration of the clay minerals as well.

Three actual examples (Figures 3, 4, and 5) are included from the writers' study of the Florena shale. These were selected to illustrate the variety of mineral compositions that can be handled by the form.

Sample 8-1 is an argillaceous dolomite, sample 14 - it is an argillaceous limestone, and sample 19-Z a calcareous shale.

Table 1

Comparison of observed and computed insoluble residue percentages in six samples of Florena shale.

Sample No.	Computed Clay and Chert	Observed Insoluble residue	Difference
10-1	36.5	34.9	+1.6
10-2b	53.4	51.6	+1.8
10-2d	56.7	56.9	-0.2
10-4a	38.0	35.2	+2.8
10-4c	44.2	46.9	-2.7
10-4e	43.4	46.0	-2.6

Average difference:

+0.7

Table 2

Minerals identified in the Florena shale

Technique	Minerals identified
Binocular microscope	Apatite Calcite Chert Hematite Pyrite
Potassium ferricyanide stain	Ankerite
Petrographic microscope	Albite Calcite Chert Dolomite
D. T. A.	Calcite Dolomite Illite Montmorillonite Quartz
X-ray diffraction	Fine-grained potassium mica Illite-montmorillonite interlayer mixture (Chlorite and kaolinite <u>not</u> present)

Table 3

Chemical compositions used in calculating mineral components of the Florena shale

Mineral Observed	Composition
Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$
Ferrodolomite	$CaO \cdot FeO \cdot 2CO_2$
Apatite	$3CaO \cdot P_2O_5$
Calcite	$CaO \cdot CO_2$
Chert	SiO_2
Dolomite	$CaO \cdot MgO \cdot 2\ CO_2$
Hematite	Fe_2O_3
Illite	$2K_2O \cdot 3\ MgO \cdot (Al_2O_3, Fe_2O_3)_8 \cdot 24\ SiO_2 \cdot 12H_2O$
Montmorillonite	$(Al_2O_3, Fe_2O_3)_2 \cdot 8SiO_2 \cdot 2H_2O$
Pyrite	FeS_2
Sericite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
Assumed	
Gypsum	$CaO \cdot SO_3 \cdot 2H_2O$
Sepiolite	$2MgO \cdot 3SiO_2 \cdot 4H_2O$
Sphene	$CaO \cdot TiO_2 \cdot SiO_2$