COMPOSITION AND CHARACTERISTIC OF CHLORITE DOMINANT SEDIMENTS OF LOWER SIWALIKS

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ABSTRACT

The quantitative mineralogical analysis was carried out on silt and clay fraction of the samples collected from Ranibagh (a location in lower Siwaliks). The chemical analysis was supported by the X-ray diffraction analysis, and other standard mineralogical analysis procedures including thermogravimetric and selective dissolution analysis. Chlorite and mica were found to be dominant minerals in silt and clay fraction. Mica content ranged from 14.70 to 17.50 percent and chlorite from 63.75 to 70.65 percent in the samples. Other minerals present were vermiculite, feldspar and quartz, though their contents were low. The chemical formulae of these chlorites were derived on the basis of elemental analysis and X-ray diffraction data. The validity of the chemical formulae assigned were established on the basis of the observed mineral properties including the actual hydroxyl water loss, CEC and electroneutrality. These determined values coincided well with the values obtained theoretically based on the assigned chemical formulae. The chlorite was found to be trioctahedral.

INTRODUCTION

The alluvial fan deposits as well as the outwash plains adjacent to lower Siwaliks region contain appreciable amounts of chlorite in the silt and clay fraction (AHMED, 1973; SINGH, 1974). Since very little information is available on the nature of these chloritic materials, it was considered worthwhile to study and characterize the chlorites in the alluvial and colluvial deposits of the outer Siwaliks where beds of chlorite rich sediments are come across. These samples were collected near Ranibagh (29° latitude and 79° 33' E longitude and at the altitude of 542 meters above the mean sea level) on the Kathgodam-Nainital road just above the northern bank of Gola river. As every where else among Himalayan chains, only Tertiary deposits are involved in the foothill belt. The foothill belt in this region is built entirely of Siwalik sediments which are widely spread along the Kumaon foothill. The lower Siwaliks show an alteration of massive soft, green and brown sandstones with chocolate to green somewhat concretionary clay. A coarse current bedding is found in the sandstones and together with the clays, they are often streaked with purple, lending a purplish aspect to whole formation and distinguishing it from the overlying middle and upper Siwaliks. In the eastern foothills the lower Siwaliks are well exposed along the Kathgodam—Nainital road. They consist of variegated (violet, red and green) clays, often concretionary and nodulous, and thick to well bedded partly calcareous sandstones.

Presence of chlorite along with illite in the foothill soils of lower Siwaliks and Himalayan ranges have been reported earlier (GUPTA, 1968 ; SEHGAL, 1973). HURELBRINK AND FEHRENBACHER (1970) who studied the alluvial fan deposits below the lower Siawliks, in the area very close to the region under study, reported the presence of large amounts of chlorite in the clay and silt fractions of the soils. The structure of chlorite was first suggested by PAULING (1930). Later ROBINSON AND BRINDLEY (1948), BROWN AND BAILEY

(1962) further studied the mineral and considerably amplified knowledge of the chlorite structure and the variation of polymorphic forms. The structure consists of alternate mica-like and brucite-like layers. The layers are continuous in the 'a' and 'b' directions and are stacked in 'c' directions with basal cleavage between the layers. The mica-like layers are trioctahedral with the general composition $(OH)_4(Si\ Al)_8(Mg\ Fe)_6\ O_{20}$. The brucite-like layer has the general composition $(Mg\ Al)_6(OH)_{12}$. The mica layer is unbalanced by substitution of Al^{3+} for Si^{4+} and the deficiency charge is balanced by an excess charge in the brucite sheet as a consequence of substitution of Al^{3+} for Mg^{2+}. Various members of chlorite group differ from each other in the kind and amount of substitution within the brucite layer and the tetrahedral and octahedral positions of mica layers. They also differ in the detailed orientations of successive octahedral and tetrahedral layers, in the relation of the mica to brucite layers, and in the stacking of successive chlorite units. Available data seem to suggest that clay mineral chlorites differ from well crystallized material in a somewhat random stacking layers and perhaps in some hydration. Unfortunately chlorite in clay material is generally found intimately mixed with other minerals so that diffraction data permit only identification of a 14 Å non-expanding mineral and not the polymorphic form. In the present study, an attempt has been made to characterize the chlorite of sedimentary origin found in the outer fringes of lower Siwaliks. The study includes data on elemental composition, chemical formulae and substituents in the basic frame work.

MATERIAL AND METHODS

Samples of sediments were collected from four spots in Ranibagh area in the exposed section of colluvial deposits along the Gola river, which cuts through the lower Siwalik sediments. The sediments were light green to bluish green in colour and were distinguishable from surrounding materials by their colour and texture. This vein in the deposit varied in thickness from 2 meters to 5 meters and was essentially coarse grained in texture containing about 5 to 7 percent clay and 10 to 12 percent silt.

The samples were air dried, crushed with a wooden roller and passed through a 2 mm sieve. The pretreatments for fractionation are indicated in the flow sheet (Fig. 1). Gravity sedimentation technique (JACKSON, 1956) was used for the separation of clay and silt fractions. Quantitative mineralogical analysis was undertaken using recent analytical techniques (RAMAN & GHOSH, 1974).
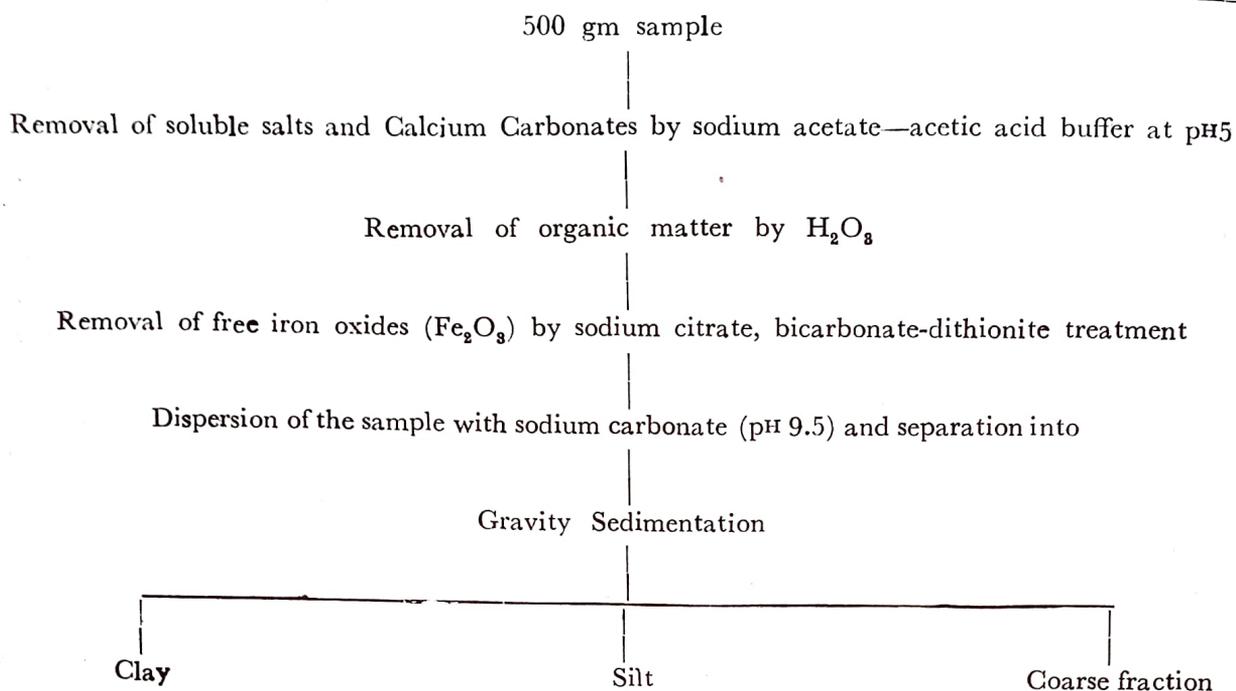
X-RAY DIFFRACTION ANALYSIS

A qualitative information on the nature of minerals present in the samples was obtained by X-ray difffraction analysis. A parallel orientation mount was prepared by drying the suspended colloid under conditions suitable to cause the basal planes to become oriented parallel to the supporting surface. Two parallel orientation specimen were prepared, one Mg—saturated glycerol solvated sample and the other K-saturated sample to be employed for the heating treatments. The X-ray diffraction pattern of Mg-glycerol sample was recorded at room temperature. The X-ray diffraction pattern of K-saturated slide was recorded at room temperature and after heating to 300°C and 550°C. The heat treatments were given for a period of 2 hours. Diffractograms were recorded in a Philips PW/1130/00/60 model X-ray diffractometer.

The random powder X-ray pattern were also recorded. The powdered clay sample was filled right up to the top in a special aluminium slide with a rectangular cavity (2 mm deep) in the centre. After packing the surface of the powder sample was

Figure 1

Flow sheet showing various pretreatments followed during particle size fractionation of sample

500 gm sample
|
Removal of soluble salts and Calcium Carbonates by sodium acetate—acetic acid buffer at pH5
|
Removal of organic matter by H_2O_8
|
Removal of free iron oxides (Fe_2O_8) by sodium citrate, bicarbonate-dithionite treatment
|
Dispersion of the sample with sodium carbonate (pH 9.5) and separation into
|
Gravity Sedimentation
|

Clay   Silt   Coarse fraction

brushed gently using a soft camel hair brush in order to bring the randomness in the sample. The dioctahedral and trioctahedral nature of the chlorite was checked by recording the (060) reflections.

DETERMINATION OF MICA

The total potassium content was determined by HF-HC10$_4$ digestion. The potassium content was determined by flame photometer. The percent K_2O was utilized in the calculation of mica on the basis of a content of 10 percent K_2O in mica, after deducting the potassium content of K-feldspars.

VERMICULITE AND SMECTITE

The determinations were based on the cation exchange capacity (CEC) with and without potassium fixation as described by ALEXIADES AND RACKSON (1965). The CEC (Ca/Mg) was first determined by saturating the exchange sites on the clay and silt samples with calcium and then replacing them with magnesium. The calcium content in the lechate was quantitatively determined by the atomic absorption spectrophotometer. The CEC (K//NH$_4$) was determined after saturation of exchange sites with potassium, drying the sample overnight at 110°C to ensure the potassium fixation by the vermiculite material and replacing the unfixed potassium from the non vermiculite material with ammonium ion. The potassium in the lechate was estimated quantitatively in a flame photometer. Mica, vermiculite and smectite contents were calculated from these data by the procedures described by ALEXIADES AND JACKSON (1965).

ALLOPHANE AND KAOLINITE

Selective dissolution analysis (SDA) of HASHIMOTO AND JACKSON (1960) was adopted to determine the allophane. The method includes the dissolution of the amorphous material by boiling the sample with 0.5 N NaOH for 2.5 minutes and rapidly cooling it. The

dissolved Si and Al were estimated colorimetrically. Based on a 10 percent water content in allophanes, can be calculated from the expression :

$$\% \text{ Allophane} = \frac{\%SiO_2 + \%Al_2O_3}{0.9}$$

On heating to 550°C kaolinite is dehydroxylated and turns amorphous. The amorphous material (obtained after heating the sample for 6 hours at 550°C) was dissolved in 0.5 N NaOH, as in case of allophane and Si and Al content were determined.

$$\% \text{ Kaolinite} = [\% (SiO_2 + Al_8O_3) - (\% SiO_2 + \% Al_2O_3)] \times 1.14$$
$$\text{After dehydro-} \qquad \text{Before dehydroxylation}$$
$$\text{xylation}$$

Here the factor 1.14 takes into account the structural OH water content of Kaolinite (14%).

CHLORITE

Thermogravimetric analysis (TGA) was followed in the determination of chlorite. Chlorite content was calculated by determining the ignition weight loss between 300°C and 950°C after correcting for the hydroxyl water content of other minerals already estimated and also taking into account the increase in weight by the oxidation of Fe^{2+} (ALEXIADES & JACKSON, 1967). Ferrous iron was determined by the method of ROTH et al. (1968).

QUARTZ AND FELDSPAR

Estimation of quartz and feldspar was done by sodium pyrosulfate fusion. The treatment decomposes mica and other layer silicates common in soils. The layer silicate relics are dissolved by alternate acid alkali treatment leaving quartz and feldspars as residues. Feldspars are determined by the allocation of K, Na and Ca in the residue to the equivalent end member feldspars after applying suitable correction factors for mineral solubility and for increase of Na from pyrosulfate in K and Ca feldspar. The remainder of the residue is allocated to quartz (KEILY & JACKSON, 1965).

ELEMENTAL ANALYSIS

Semimicro samples (0.100 gm) were analysed for their content of Si, Fe^{2+}, Fe^{3+}, Ca, Mg, K, Na and Al by spectrophotometric procedures. In the general plan, the analytical system makes use of two 0.100 gm samples, one of which is decomposed by heating with HF-HClO$_4$ and the other by fusion with Na_2CO_2. The sample decomposed by HF—HClO$_4$ is used for the determination of K, Na and Mg. The Na_2CO_3 fusion is used for the Si and Al determination (JACKSON, 1956).

The silicon in Na_2CO_3 fusion was determined colorimetrically by the molybdosilicic acid yellow colour method (JACKSON, 1958). Aluminium was determined by aluminon method described by HSU (1963).

The ferrous and ferric iron were determined by the modified procedure of ROTH et al. (1968). This procedure eliminated the difficulties encountered in the estimation of ferrous iron due to its rapid oxidation during chemical analysis.

The sodium and potassium were determined by the flame esmission spectrophotometer and calcium and magnesium contents by atomic absorption spectrophotometer.

CALCULATION OF CHEMICAL FORMULA OF THE MINERAL

The calculation of the chemical formula of layer silicates is a matter of elemental ratios. The procedure is to equate the oxygen atoms to the number in unit cell and then to derive the corresponding proportion and number of cations present from the elemental analysis. The percentages of cations are converted to equivalents per 100 gm and then the sum of equivalents of positive charge in ratio to the total negative charge gives a factor from which the moles of cations per formula weight can be calculated. The total equivalents (E) of cations per formula weight is 56 in this case. The chemical formula for these samples were calculated by the method given by JACKSON (1956).

RESULTS AND DISCUSSION

All the samples studied showed a similar X-ray diffraction behaviour. A representative pattern of sample number 4 is given in Fig. 2. All the samples studied showed a
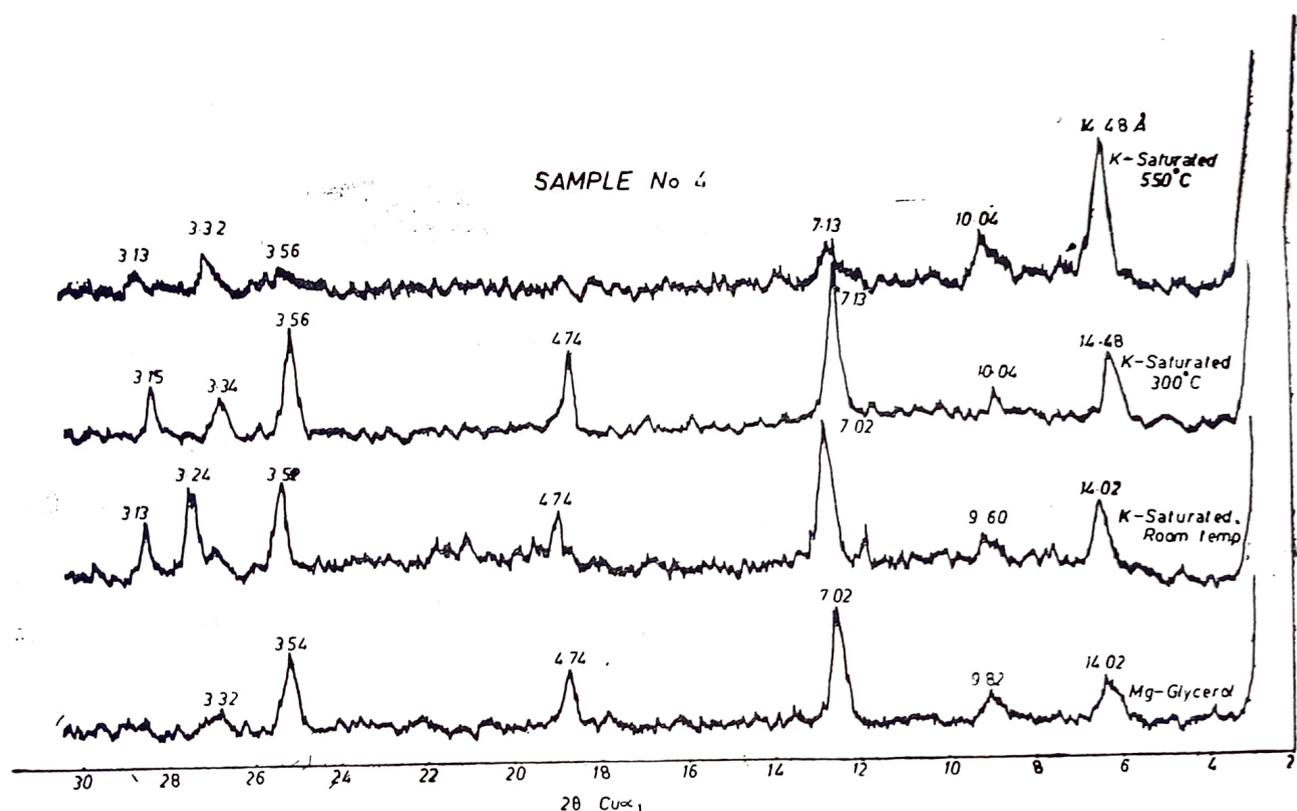

Figure 2. Mineralogical studies on sediments from lower Siwaliks. Part I. Mineralogy of size fractions of chlorite dominant sediments.

strong difffaction peak at 14 Å which did not change in intensity appreciably on K-saturation or heating. This confirmed that the dominant mineral fraction in the sample was chlorite. The samples also showed a peak at about 10 Å indicating the presence of mica. Kaolinite and smectite were absent in the sample, which was later confirmed by quantitative analysis procedures.

Quantitative mineralogy of the samples

The basic data from which the mineral contents were estimated are given in Tables 1 and 2. The mineral composition calculated from this data is given in Table 3. In both

Table 1—Total K_2O content, K_2O content in K-feldspar and CEC values of clay and silt fractions

Sample No.	Total K_2O (percent)		K_2O attributed to K—feldspar (percent)		CEC Ca/Mg me/100 gm.		CEC K/NH_4 me/100 gm	
	Clay	Silt	Clay	Silt	Clay	Silt	Clay	Silt
1	1.68	1.75	0.21	0.18	5.50	4.40	5.12	
2	2.05	1.99	0.30	0.26	4.50	3.60	4.36	2.56
3	1.81	1.93	0.31	0.24	4.75	4.10	4.36	2.87
4	1.87	1.93	0.29	0.19	4.75	4.00	4.48	2.82

Table 2—Selective dissolution and water loss on heating data

Sample No.	% K_2O, Na_2O and CaO in residue after $Na_2S_2O_7$ fusion			S_2O_2 and Al_3O_3 percent after NaOH dissolution		Percent water loss		% FaO
	K_2O	Na_2O	CaO	SiO_2	Al_2O_3	A*	B*	
				clay				
1	4.99	0.67	2.39	3.42	0.58	9.89	1.50	8.7
2	5.71	0.66	2.77	3.41	0.48	9.02	1.12	11.5
3	6.03	0.70	2.82	3.41	0.52	8.82	1.00	10.0
4	6.00	0.63	2.66	3.42	0.65	8.92	1.15	10.6
				Silt				
1	6.10	0.60	4.50	2.66	0.46	9.51	1.00	8.7
2	7.59	0.86	4.50	1.82	0.42	9.73	1.11	11.5
3	7.50	0.46	4.64	1.82	0.31	9.59	0.95	10.0
4	4.73	0.51	4.22	1.52	0.36	9.60	0.94	10.6

A* Total water loss between 300—950°C.
B* Water loss above 300°C by minerals other than chlorite.

the clay and silt fractions, chlorite and mica were the dominant minerals followed by K fedspar, allophane and quartz.

Vermiculite and Smectite

Only negligible amounts of vermiculite were present in the clay and silt fractions. Vermiculite content ranged from 0.10 to 0.32 percent in clay and 0.68 to 0.86 percent in

Table 3—Mineralogical composition of clay and silt fractions (Values expressed in percentage)

Sample	Chlorite	Mica	Allophane	K-feldsapr	Ca feldspar	Quartz	Vermiculite
Clay							
1	69.37	14.70	4.44	2.74	0.62	1.97	0.32
2	65.50	17.50	4.33	3.93	0.91	2.06	0.10
3	63.75	15.00	4.36	4.07	0.91	1.88	0.26
4	63.87	15.80	4.51	3.89	0.82	1.85	0.18
Silt							
2	70.65	17.30	2.48	2.17	0.71	0.98	0.68
3	69.60	16.90	2.36	2.02	0.69	0.92	0.80

silt fractions. Smectite was absent. These are borne out in X-ray diffraction data also discussed earlier.

Feldspar and quartz

The percent K-feldspar ranged from 2.74 to 4.07 percent in the clay fraction and 1.54 to 2.17 percent in silt fraction. Ca-feldspar content was much less ranging from 0.62 to 0.91 percent in clay and 0.63 to 0.71 percent in silt fraction. Na-feldspar was absent. The quartz content varied from 1.85 to 2.06 percent in the clay fraction and 0.92 to 1.30 per cent in the silt fraction.

Allophane

The allophane content varied from 4.33 to 4.51 percent in the clay fraction and 2.05 to 3.47 percent in silt fraction. Allophane content was relatively more in clay fraction than in the silt fraction. Allophane gives a porous structure in the soils and sediments predisposing them to high permeability and exhaustive leaching.

Mica

The mica content varied from 14.70 to 15.80 percent in clay fraction and 15.70 to 17.40 percent in the silt fraction. The mica in these samples was due to present material, as the lower Siwaliks are rich in micaceous schists.

Chlorite

The chlorite content varied from 63.75 to 69.37 percent in the clay fraction and 67.65 to 70.65 percent in the silt fraction. Chlorite occurred extensively in soils, mainly inherited from mafic rocks and serpentine but to some extent formed in the soils. In the lower Siwaliks of Himalayan region mafic rocks, chlorite and micaceous chist are well distributed. The source of this dominantly chlorite rich fraction containing high amounts of fine materials of clay and silt soils, would be these deposits.
The X-ray diffraction pattern of random powder rsample in all these cases showed (060) reflection persistent at about 1.54 Å. This is a characteristic feature of the trioctahedral species.
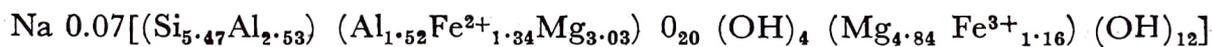
Chemical formula

The complete elemental analysis of clay fraction is given in Table 4. The chemical formulae were calculated from the data after several refinements of the original formula by

Table 4—Elemental composition of clay fraction of chlorite (Reported as percentages on oven dry basis)

Sample No.	Si	Mg	Al	Fe^{2+}	Fe^{3+}	K	Na	Ca	OH water loss Observed	OH water loss Calculated	CEC me/100 gm Observed	CEC me/100 gm Calculated
1	13.70	14.70	8.60	6.75	4.55	1.40	1.20	0.31	11.01	11.50	5.50	5.9
2	16.00	14.40	7.70	8.90	0.99	1.70	1.35	0.24	11.60	11.62	4.50	5.1
3	17.00	14.40	7.70	7.75	1.25	1.50		0.29	11.46	11.78	4.75	5.2
4	15.20	12.60	8.60	8.20	1.90	1.55	1.30	0.36	11.02	11.93	4.75	4.4

taking into account the impurities present in the sample. The corrections were made especially for mica and K-feldspars present in the sample and estimated quantitatively by independent methods. While making refinements in chemical formulae, it was assumed that the mica was present in the biotite form. This assumption is based on the high amounts of Fe^{2+} and Mg present in the sample. The chemical formulae calculated after all the refinements and based on this data are presented below :
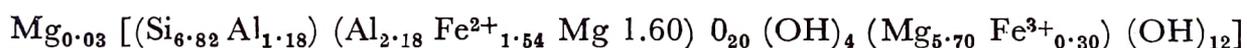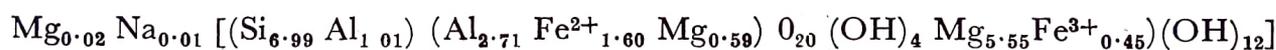
Sample 1

$$Na_{0.07}[(Si_{5.47}Al_{2.53})\,(Al_{1.52}Fe^{2+}_{1.34}Mg_{3.03})\,O_{20}\,(OH)_4\,(Mg_{4.84}\,Fe^{3+}_{1.16})\,(OH)_{12}]$$

Sample 2

$$Mg_{0.01}\,Na_{0.04}[(Si_{6.43}\,Al_{1.57})\,(Al_{1.94}\,Fe^{2+}_{1.86}\,Mg_{1.87})\,O_{20}\,(OH)_4\,(Mg_{5.77}\,Fe^{3+}_{0.23})(OH)_{12}]$$

Sample 3

$$Mg_{0.03}\,[(Si_{6.82}\,Al_{1.18})\,(Al_{2.18}\,Fe^{2+}_{1.54}\,Mg\,1.60)\,O_{20}\,(OH)_4\,(Mg_{5.70}\,Fe^{3+}_{0.30})\,(OH)_{12}]$$

Sample 4

$$Mg_{0.02}\,Na_{0.01}\,[(Si_{6.99}\,Al_{1.01})\,(Al_{2.71}\,Fe^{2+}_{1.60}\,Mg_{0.59})\,O_{20}\,(OH)_4\,Mg_{5.55}Fe^{3+}_{0.45}(OH)_{12}]$$

It will be noted that Mg and Fe^{2+} filled the available octahedral positions both in 2 : 1 layer silicate sheet and in the brucite layer. Since the octahedral positions are predominantly occupied by the divalent species the mineral is a trioctahedral chlorite.

The electrical charges are balanced properly in all the sample formulae. This further suggests that the assigned chemical formulae represent the stable form of the mineral.

The cation exchange capacity (CEC) was determined experimentally, as well as theoretically based on the assigned chemical formulae. It is found that both the CEC values coincide fairly well (Table 4). This adds to the validity of the chemical formulae assigned to the mineral samples. In another experiment the hydroxyl water loss was determined experimentally and theoretically based on the assigned chemical formulae of the mineral sample. The corrections were made for the water loss due to minerals present other than chlorite and also for the weight gain because of the oxidation of ferrous iron to ferric form.

The corrected values of hydroxyl water loss determined experimentally were found coinciding fairly well with the values calculated from assigned chemical formulae. Hence, the assigned chemical formulae suited well to the mineral sample in explaining the CEC, hydroxyl water loss and overall electroneutrality of the samples. It is further observed that in all the formulae the total number of units are not equal to 12 in both the sections. Hence, there may be some vacancies in either of the two octahedral positions.

Free energy of formation

Knowledge of the chemical formulae for minerals is very useful not only in understanding the mineral properties but also for judging the degree of isomorphous substitution in various units. This gives information on the environment during the formation of mineral as well as its stability. The Gibbs free energy of formation ($\triangle G^{\circ}{}_{f}$) of samples were calculated using the above chemical formulae. $\triangle G^{\circ}{}_{f}$ values of these ranged from —15179.5 K Joules mole^{-1} to —15384.5 K Joules mole^{-1}, as compared to a standard reference chlorite sample which had $\triangle G^{\circ}{}_{f}$ —14099.6 K Joules mole^{-1} (AGNIHOTRI *et al.* (1979).

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