

Appendix-I

Weathering of Plagioclase Feldspars in Different Environments
in Deccan Traps : Observations Based on SEM Studies*

L. K. Kshirsagar

Department of Geology
University of Poona
Pune 411 007, India

* Paper presented, and to be published in the Proceedings
of the 'Symposium on Three Decades of Development in
Petrology, Mineralogy and Petrochemistry in India', Jaipur,
May 1981.

Abstract

Weathering of plagioclase feldspars derived from the rocks of basaltic composition belonging to the Deccan Trap volcanism, in three different environments namely :

- (i) the tuffs and clayey material occurring within the interflow zones;
- (ii) the river sediments - as products of weathering - ;
- (iii) the saprolite zone in a laterite profile;

was studied using scanning electron micrographs. It is observed that their modes and products of weathering differ substantially. These observations are presented with the help of a set of SEMs.

In class (i) weathering seems to be initiated by solution along certain crystallographic directions and available microcracks, resulting finally into neomineralization of distinct montmorillonite phase. In this environment the process is largely controlled by surface reactions with organic acids. The principal mode of weathering of plagioclase of class (ii) appears to be a high degree of dissolution followed by fragmentation along cleavage planes

during mechanical transport. Some montmorillonite appears at a late stage. In the third environment the weathering has commenced with dissolution without precipitation but has ultimately given rise to grainy gibbsite and poorly crystalline kaolinite.

Plagioclase feldspars, mostly of the labradorite variety amount to nearly 50 % by volume in the basaltic rocks of the Deccan Traps. Though weathering of basaltic rocks in Deccan Traps has been studied for quite some time, (Valeton, 1967; Tomar and Rosenqvist, 1975; Bhattacharya and Sinha, 1976) observations regarding weathering of individual minerals are not many, and weathering studies on plagioclases from these rocks in India are lacking. An attempt is made to record the weathering stages of plagioclase feldspar in different environments, as observed under a scanning electron microscope (SEM).

Material and Methods

Samples from three different environments classified as under :

- (i) the tuffs and clayey material occurring within the interflow zones,

- (ii) the river sediments - as products of weathering -,
and
- (iii) the saprolite zone in a laterite profile
were studied using SEM.

The samples from (i) and (ii) are from the Pune (Lat. $18^{\circ}32'N$; Long. $73^{\circ}51'E$; Alt. 559 m) area where a tropical, monsoon, subhumid - dry type climate exists. Annual rainfall is approximately 50 cm concentrated in the four months between June and September. Mean annual temperature is $25^{\circ}C$. The material from class (ii) is collected from the Mula river sediments. These clays are presently used for the manufacture of earthen ware. Samples of class (iii) belong to a saprolite zone below laterite capping at Mahabaleshwar (Lat. $17^{\circ}56'N$; Long. $73^{\circ}40'$; Alt. 1382 m). Climate of Mahabaleshwar is typically tropical, monsoon, and perhumid type. Annual rainfall is over 500 cm and is concentrated in the same four months but the number of rainy days are much more than that in the Pune area. Mean annual temperature is $20^{\circ}C$.

Samples representing environments mentioned above were scanned using a S4-10 STEREOSCAN SEM, manufactured by Cambridge Scientific Instruments Ltd.

Freshly broken chips of specimens blown clean of dust with light airblow were mounted on aluminium stubs, using a high conductivity paint. Samples were coated by Au/Pd alloy of about 100 Å^o thickness under a vacuum of 0.5 to 0.7 torr and using a current of 20 mA in a period of about 2.5 minutes. The sputter ion coating method was preferred to other vacuum devices since it gives a more uniform coating. Samples from class (iii) were unstable under electron bombardment and destroyed the coating. Hence to avoid the charging effect thus caused, they were heated before coating in an oven for three hours at 50 °C and then scanned.

Results :

Plagioclase in class (i) : Figures 1 to 4 show a sequence of alteration from a fresh grain to neomineralized montmorillonite. Fig.1 shows an angular plagioclase with one vertical microcrack and a few at right angle to it. Some alteration along these cracks has taken place. This is evidenced by few light toned patches. Rest of the grain appears fresh. Fig. 2 shows effects of dissolution; a rough, irregular surface is developed. Neither amorphous coating nor any neomineralization is seen. Fig. 3 shows enlarged portion of a microcrack showing fine smectite type

clays developed along the walls. These smectite type clays are montmorillonites as seen from the enlarged portion of the same area (Fig. 4).

In some feldspar grains parallel crescent shaped notches are seen. Several thousand notches, arranged parallel to each other could be observed. Only a small magnified region from the area is seen in Fig. 5. The parallel arrangement of notches and the smectite crystals formed in these notches are clearly visible. Absence of any fine grained protective layer in Figs. 1 to 5 is striking.

Plagioclase in class (ii) : Fig. 6 shows much dissolved plagioclase grain viewed obliquely to the cleavages. Grain is seen to weather into small blocks giving a staircase like appearance to it. Only in the right bottom corner some smectite has formed. Amorphous coating is absent.

Plagioclase in class (iii) : Quite a different sequence of weathering stages is observed in plagioclases of this class. Fig. 7 shows relatively fresh feldspar. Only the portion on the right shows some alteration. Developments of micro-cracks and alteration along them is observed in Fig. 8. Central portion of the grain is fresh while it has altered

to kaolin type clays along the outer parts. Fig. 9 shows an enlarged portion of the same grain. Microcracks and boundary between altered and unaltered parts is more distinct.

Characteristic dissolution pitting is seen in Fig. 10.

Incipient deposition of amorphous material and some grainy gibbsite may be noted. A more advanced stage of dissolution pitting and deposition of grainy gibbsite is seen in Fig. 11. Here only some tabular or bar shaped mesh of feldspar coating with grainy gibbsite is seen.

Entire surface of the feldspar grain coated with grainy gibbsite and some widened cleavages, again filled in by gibbsite and some amorphous material is shown in Fig. 12. As final product of weathering in this environment on one hand one gets production of grainy gibbsite (Fig. 13) and on the other hand the kaolin clays (Fig. 14) with slightly crinkled edges are developed.

Discussion

In recent years natural as well as artificial weathering of feldspars has been studied by a few workers. Helgenson, 1971; Wollast, 1967; Busenberg and Clemency, 1976; have suggested that during chemical weathering of feldspars

a protective layer of aluminosilicates is developed on the mineral surface through which further diffusion of cations takes place and the observed decrease in the rate of chemical weathering of feldspars is attributed to the formation of aluminosilicate coating. Lagache (1976), and Berner and Holdren (1977) are of the opinion that the reactions that occur at the interface between aqueous solutions and relatively fresh feldspar control the chemical decay. Weathering of plagioclase from a porphyritic granite in Belitung has been studied by Murray (1975). He has shown that plagioclase alters to residual kaolin directly within five cm from fresh rock.

Lange (1976) has given a sequence of weathering of feldspars using SEMs. First solution structures appear without newly formed minerals, followed by X-ray amorphous hydroxides and later formation of hydrosilicates and development of clay minerals. Page and Wenk (1979) have shown the alteration of plagioclase to smectite and to sericite in alteration halo of a sulphide bearing vein in Montana using TEM and have postulated that there is a statistical match between the (001) planes of plagioclase and (001) planes of the newly formed phyllosilicates.

Rodgers and Holland (1979) have studied the alteration of feldspars along microcracks. They have divided microcracks into the weathering microcracks and the alteration microcracks. In case of oligoclase a sequence from fresh oligoclase to smectite to kaolinite is observed within the microcracks with sharp boundaries.

In the present study weathering of plagioclase from class (i) seems to have initiated in two different modes, ending into same product, the smectite. One is along microcracks (Figs. 1 to 4) and the other is by formation of etch pits (Fig. 5). A sequence of alteration stages from unaltered fresh grain, without any coating of amorphous precipitate or clay, through differential solution pits probably along a certain crystallographic plane, giving rise to montmorillonite is observed along microcracks.

Development of oriented pits during etching on feldspars has been described by Berner and Holdern (1977), Lundstrom (1970), Seifert (1967), Parham (1969). They have observed the orientation of pits to be parallel to some crystallographic direction in a crystal. The oriented, parallel, crescent shaped pits observed in the present study are in conformity with these experimental observations of the

above workers. Dissolution by soil organic acids has probably been responsible for the formation of these pits by dissolving the Na, Ca and other cations and leaving behind hydrated aluminosilicates which recrystallised in each pit to give smectite. All stages from incipient notch to well developed crescent shaped pits with smectite crystals have been observed (Fig. 5).

The overall absence of any protective amorphous layer on grain surface suggests that the weathering of feldspars was primarily controlled by surface reactions and not by molecular diffusion or through a protective layer of precipitated amorphous material. This is in conformity with the views expressed by Berner and Holdern (1977). Presence of well crystallized montmorillonite in the microcracks appears to be a result of neomineralization probably dating later than dissolution stage since this phase is well crystallized and undisturbed.

Effects of high degree dissolution are seen in plagioclases belonging to class (ii) where deep, long cavities are seen. The principal mode of weathering is fragmentation parallel to cleavage planes caused during mechanical transport. Only a small portion in the right

hand bottom corner in Fig. 6 where the feldspar grain is thin it has directly altered to smectite, possibly due to decalcification by leaching.

The observations in class (iii) plagioclase where the same primary rock altering lines, to kaolin and gibbsite in the same environment, (Figs. 13 and 14), though appears strange, is not very uncommon. Keller (1979) has reported similar results in bauxitization sequence of a nepheline syenite in Arkansas where the primary rock bauxitizes following two trends, either via an elongate kaolin mineral or directly to gibbsite. The occurrence of kaolin and gibbsite together is however, still a puzzling problem. Kaolin may desilicate to gibbsite or even gibbsite may resilicate to kaolin. The simplest interpretation may be offered by assuming the formation of gibbsite above water table and that of kaolin below. But on the scale at which this feature is observed, dissolution and resilication from solution within small vugs (Keller, 1979) seems possible as suggested by Keller (1979). Though the mobility of Aluminium is much less at room temperature the studies by Ling and Hem (1975), Huang and Keller (1972), and Harder (1977), suggest that complexing solutions and organic acids play a vital role in precipitation.

Book type kaolin is normally formed in a geochemically stable, long duration environment, in a low lying terrain and below ground water table. On the contrary, elongates are known to have formed in a high land region with fluctuations of ground water table. (Keller, 1977). The environment that prevails at Mahabaleshwar is typically high land type, and the permanent water table is below the saprolite zone at the saprolite-hardrock interface. Only in the rainy seasons it rises higher in the clay zone. The observed predominance of flaky kaolin in the clays from Mahabaleshwar could be an interaction of this typical environment and also due to the difference in the parent material, which is plagioclase in the present study and it is K feldspars in the weathering zones which Keller has studied. The crinkled edges of kaolin flakes (Fig. 14) are indicative of recrystallization (Keller, 1977).

The observations made during present study may be summarized as follows :

In general, during the weathering of plagioclase there is an absence of kaolin books and elongates, halloysite is not seen; and amorphous coating is rare. Smectite observed in the tuffs is well crystalline. Well

crystallized kaolin or gibbsite is absent in the saprolite environment, though some recrystallisation of kaolin has taken place. The normally expected sequence of alteration to kaolin through smectite is not seen in plagioclases from saprolite.

The study shows that, there exists a delicate geochemical balance which enables coexistence of both kaolinite and gibbsite irrespective of ground water table, on a microscale. In the natural weathering of plagioclase studied in the present case no significant coating has been observed. This brings out two significant points (1) solution by surface reactions appears to be dominant process rather than molecular diffusion; and (2) rate of chemical weathering of plagioclase in natural open system is directly related to the nature of weathering solutions and the microenvironments.

Acknowledgements

The author is highly grateful to the Director, I.P.E., Dehra Dun for giving permission to work on SEM. The author expresses his gratitude to Dr. N. Bhattacharya and Dr. P. G. Kale of I.P.E., Dehra Dun, who extended their

unreserved help in the SEM studies. The author expresses his sincere thanks to Prof. K.B. Powar, Head of the Department of Geology, University of Poona for kindly providing the facilities. Thanks are due to Dr. A.V. Phadke, Department of Geology, University of Poona, for his valuable guidance and critically reviewing the manuscript. Financial assistance given by C.S.I.R. through Senior Research Fellowship is gratefully acknowledged.

References

- Berner R.A. and Holdren G.R., (1977), Mechanism of feldspar weathering : Some observational evidence, Geology, V.5., p. 369-372.
- Bhattacharya, N. and Sinha A.K. (1976), Weathering of Deccan Trap basalts and genesis of clay minerals, Ind.J.Earth.Sci. V. 3.,, p. 148-159.
- Busenberg, E., and Clemency, C.V. (1976), The dissolution kinetics of feldspar at 25°C and 1atm CO₂ partial pressure, Geochim et Cosmochim Acta, V.40, p. 41-50.
- Harder, H., (1977), Clay mineral formation under lateritic weathering conditions, Clay Minerals, V.12,p.281-288.
- Helgenson, H.C., (1971), Kinetics of mass transfer among silicates and aqueous solutions, Geochim et Cosmochim Acta, V. 35, p. 421-469.
- Huang, W.H., and Keller, W.D. (1972) Geochemical mechanics for the dissolution, transport, and deposition in the zone of weathering, Clays, and Clay Minerals, V.20, p. 69-74.
- Keller, W.D., (1977), Scan electron micrographs of Kaolins collected from diverse environments of origin-IV. Georgia kaolin and kaolinizing source rocks. Clays and Clay Minerals, V. 25, p. 311-345.

- Keller, W.D., (1979), Bauxitization of Syenite and diabase illustrated in scanning electron micrographs, Economic Geology, V.74, p. 116-124.
- Lagache, M., (1976), New data on the kinetics of the dissolution of alkali feldspar at 200° in CO₂ charged water, Geochim et Cosmochim Acta. V. 40, p. 157-161.
- Lange, P., (1975), Scanning electron microscopical examination of weathered rocks, International Kaolin Symposium, Dresden, Abstracts, p. 34.
- Lind, C.J., and Hem, J.D., (1975), Effects of organic solutes on chemical reactions of aluminum, U.S.Geol. Survey Water Supply Paper 1827-G, pp. 83.
- Lundstram, I., (1970), Etch pattern and albite twinning in two plagioclases, Arkiv.Mineralogi och Geologi,V.5,p.63-91.
- Murray, H.H., (1975), Alteration of a granite to kaolin-Mineralogy and geochemistry, International Kaolin Symposium, Dresden, Abstracts, p. 19.
- Page, R., and Wenk, H.R., (1979), Phyllosilicate alteration of plagioclase studied by transmission electron microscopy, Geology, V. 7, p. 393-397.
- Parham, W.E., (1969), Formation of halloysite from feldspar : low temperature, artificial weathering versus natural weathering,Clays and Clay Minerals, V.17, p. 13-22.

Rodgers, G.P., and Holland, H.D., (1979), Weathering products within microcracks in feldspars, Geology, V.7, p. 278-280.

Seifert, K.E., (1967), Electron microscopy of etched plagioclase feldspar, Am.Ceramic.Soc.Jour., V.50, p.660-661

Tomar, K.P., and Rosenqvist, I.Th., (1975), Mineralogical composition of a deep black soil profile of India : cation saturation effect on DTA curves of a smectitic mineral, Lithos, V.8, p. 269-274.

Valeton, I., (1967), Bauxitfuhrende laterite auf dem Trappbasalt Indiens als fossile polygenetisch veranderte bodenbildung, Sediment. Geol., V.1, p. 7-56.

Wollett, R., (1967), Kinetics of the alteration of K-feldspar in buffered solutions at low temperature, Geochim et Cosmochim Acta, V. 31, p. 635-648.

Appendix - II

Mineral composition indicated by all techniques combined

<u>Sample No.</u>		<u>Technique used</u>
F 2	Smectite group of minerals, mix layer minerals	DTA
F 3	labradorite, illite-montmorillonite mix layer, montmorillonite-chlorite mix layer	DTA, IR
F 4	montmorillonite-illite mix layer, montmorillonite chlorite mix layer	DTA
Ch 2	montmorillonite, mix layer minerals	DTA
Ch 3	montmorillonite, mix layer minerals	DTA
Ch 4	montmorillonite, mix layer minerals	DTA
Ch 5	montmorillonite-chlorite (more) + illite-montmorillonite	DTA, SEM, IR
NCL 1	labradorite, mix layer group minerals	DTA
NCL 2	labradorite, mix layer minerals	DTA
Sg 1	montmorillonite, labradorite, heulandite, hectorite(?)	XRD, IR
Sg 2	labradorite, montmorillonite, heulandite	XRD
Sg 5	montmorillonite with expandible layers, illite-montmorillonite, little kaolinite, very less hematite	XRD
Sg 6	montmorillonite-chlorite, montmorillonite, illite-montmorillonite, illite, + little-calcite, hematite, magnetite hectorite(?) kaolinite(?)	XRD, IR
Sg 7	montmorillonite - with mixed layers	XRD
Sg 8	montmorillonite with expandible layers + doubtful kaolinite	XRD
K 6	montmorillonite (mix layered) and labradorite	XRD
Sh 4	montmorillonite-chlorite irregular, illite-montmorillonite, montmorillonite, some labradorite, little calcite, magnetite and ilmenite	DTA, XRD, SEM, IR
PSN 1	montmorillonite, illite-montmorillonite, illite	XRD
PB 1	chlorite lb, illite-montmorillonite, montmorillonite, little calcite, very less nontronite	XRD
Psr 1	montmorillonite-chlorite, labradorite, some little and probably sepiolite	XRD
Cl 1	montmorillonite showing some expansion, labradorite, illite-montmorillonite, illite, calcite	DTA, XRD, SEM, IR
DW 1	montmorillonite, illite, sepiolite(?), little kaolinite	XRD
DW 3	montmorillonite-chlorite, illite-montmorillonite, montmorillonite, distinct, presence of kaolinite	XRD

Contd..

<u>Sample No.</u>		<u>Technique used</u>
SW 4	montmorillonite, little kaolinite, little gibbsite(?) some quartz and labradorite, (NaM-C or I-M)	XRD
Mtr 1	low quartz, + some montmorillonite	DTA, XRD
S 1	kaolinite, gibbsite (but heated sample gives peaks)	DTA, XRD
S 3	kaolinite	DTA, XRD, SEM, IR
KfmI	kaolinite	DTA
Kfm IV	kaolinite	DTA, XRD
DG 3	kaolinite (poorly crystalline - exo.peak, broad and asymmetric), gibbsite (?)	DTA, XRD, IR
DG 4	kaolinite + some smectite (montmorillonite)	DTA
Soil/Litho	kaolinite, some montmorillonite	DTA, XRD
4, Kengher	kaolinite + little montmorillonite, gibbsite (?)	DTA, IR
M 2	kaolinite + some illite-montmorillonite mix layer, labradorite (?)	DTA, XRD, SEM
M 4	labradorite, montmorillonite-chlorite mix layer mineral	DTA
TN 1	kaolinite, some labradorite, montmorillonite (?), gibbsite (?)	DTA, XRD, SEM, IR
Pr 2	kaolinite(?), halloysite(?), illite, illite-montmorillonite mix layer	DTA, XRD, SEM, IR
Kaolonised Trap 'a'	kaolinite, some montmorillonite	XRD.