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Discussion and comments on the paper: electron-optical studies of phyllosilicate intergrowths in sedimentary and metamorphic rocks

IN a recent paper White *et al.* (1985) discussed the origin and chemistry of phyllosilicate intergrowths in sandstones, shales, metagreywackes, and low-grade schists. They came to an important conclusion, that the origin of chlorite–illite (phengite) intergrowths is mainly by diagenetic and low-grade metamorphic alteration of detrital biotite grains. This conclusion is in good agreement with the observations of the senior author (Morad, 1986) on chlorite–mica (phengite and biotite) intergrowths in shales and sandstones from the Brøttum Formation (Upper Proterozoic; the Sparagmite region of southern Norway). The importance of this agreement in interpretation is that it gives a new view on the origin of such phyllosilicate intergrowths, a matter which is still controversial. Previously, several origins were proposed (see review by Craig *et al.*, 1982), but none could clearly account for, as biotite readily does, the source of ions and the unique pattern of intergrowth.

As experienced by White *et al.* (1985), there are difficulties in obtaining pure chlorite or mica analyses from the intergrowths by means of electron microprobe. Instead, the chlorite analyses often contain K and Ti, while illites show high Fe and Mg contents, and the biotites are greatly

depleted in K and/or Fe and Mg. Some analyses of both types of biotite from the Brøttum Formation are given in Table I. A plot of the analyses on an Al_{total}–(K + Na) binary diagram (fig. 1) reveals that those biotites which are mainly depleted in K are characterized by a gradual decrease in interlayer cations and simultaneous increase in total Al, and their general trend is toward chlorite, thus called chloritized biotites here. Most of the analyses of White *et al.* (1985) fall along this trend too (Table II). The second group of biotite analyses (Table I) show higher interlayer cation content, but also a gradual increase in total Al and their trend is toward illite, thus called illitized biotites here. Such biotite compositions, however, were not reported in the paper of White *et al.* (1985) because their analyses were restricted to a biotite grain altered into mainly chlorite, though analysis no. 1 (Table IV of White *et al.*; Table II this paper) is close to illite. The total octahedral occupancies (TOO) of these altered biotites deviate significantly from 6.00 of ideal biotite. The chloritized biotites have TOO greater than 6.00, whereas the illitized biotites have TOO much lower than 6.00, hence confirming the alteration trends above.

The statement made by White *et al.* (1985; p. 420)

Table I. Structural formulae (based on 44⁻) of altered biotites from

sandstones of the Brøttum Formation analysed by electron microprobe[x]

(analyses 1-3 chloritized biotites; 4-7 illitized biotites).

	1	2	3	4	5	6	7
Si	5.41	5.23	5.08	6.00	5.97	6.10	6.34
Al^{iv}	2.59	2.71	2.92	2.00	2.03	1.90	1.64
Al^{vi}	1.11	0.79	1.13	1.89	2.22	2.42	2.95
Fe[xx]	3.28	3.68	3.25	2.13	1.78	1.42	0.78
Mg	1.98	1.70	2.17	1.00	0.88	0.93	0.68
Ti	0.02	0.18	0.06	0.15	0.17	0.10	0.06
TOO	6.39	6.35	6.61	5.17	5.05	4.87	4.47
Na	0.00	0.00	0.16	0.00	0.03	0.07	0.07
K	0.60	0.88	0.29	1.46	1.33	1.41	1.62

x)microprobe analyses were done on an ARL-EMX instrument fitted with

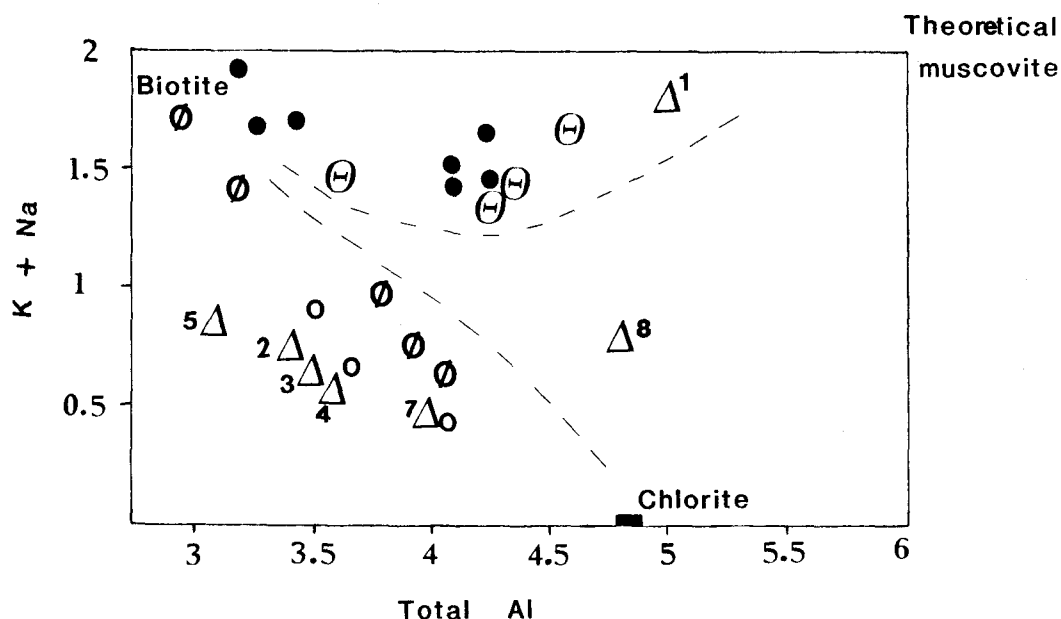a Link energy dispersive system which uses the ZAF-4 programme.

xx)Fe as Fe^{2+}.

FIG. 1. Plot of interlayer K + Na vs. total Al for phyllosilicates derived from biotites. ● = Peters and Hofmann (1984); ⊘ = Craw et al. (1982); ▲ = White et al. (1985; Table II in the present communication); ⊖ and ○ = illitized and chloritized biotites respectively (the Brøttum Formation; Table I). Analysis no. 8 is presumably a mixture of biotite, chlorite, and illite.

Table II. Structural formulae of phyllosilicate chemical analyses of White et. al. (1985; table IV and V, p.417). The formulae of analyses 1-8 are on the basis of 44⁻ and of chlorite on basis of 56⁻.
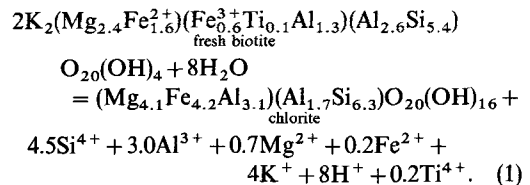
	1	2	3	4	5	7	8	chlorite
Si	6.45	4.89	4.88	4.76	5.07	5.42	5.32	6.31
Al^{iv}	1.51	3.11	3.12	3.24	2.93	2.58	2.68	1.69
Al^{vi}	3.51	0.29	0.37	0.32	0.15	1.38	2.13	3.10
Fe^{x}	0.52	3.85	3.59	3.70	3.19	2.57	2.68	4.23
Mg	0.37	2.29	2.43	2.59	2.95	2.38	1.77	4.10
Ti	0.10	0.33	0.31	0.31	0.33	0.02	0.11	
T00	4.51	6.76	6.70	6.92	6.62	6.35	6.69	11.43
Na	0.07	0.00	0.04	0.07	0.09	0.09	0.07	
K	1.75	0.73	0.58	0.48	0.76	0.37	0.72	

x Fe as Fe^{2+} (except analysis no. 1 where Fe is as Fe^{3+})

that 'biotite to chlorite change proceeds via an intermediate K-depleted biotite' is disputable. Analyses of the biotites (analyses 1-3, Table I; analyses 2-7, Table II) suggest that the main change in composition of biotite by chloritization is the decrease in K content. The amount of K obtained from such biotites actually reflects the volumetric ratio of chlorite/biotite irradiated by the electron beam, rather than low K in the biotite structure. The resolution of scanning electron microscopes using the backscattered mode is not sufficient to reveal the possible, very minute (a few tens of Ångströms thick) chlorite layers in biotite, as shown for example by Veblen and Ferry (1983) by means of high resolution TEM. Therefore biotites containing variable but low amounts of K should be called chloritized biotites and not weathered biotites as suggested by White et al. (1985; p. 420) because weathering, by definition, involves processes that occur outside the regimes of diagenesis and low-grade metamorphism. Similarly, a decrease in Fe and Mg accompanied by increase in Al contents of biotite, reflect the increase in volumetric ratio of illite/phengite to biotite irradiated by the electron beam. Thus biotites showing such compositions (analyses 4-7, Table I) should be called illitized/phengitized biotites. Furthermore, the presence of relatively small amounts of K and Ti is not characteristic of chlorites derived from biotites (see White et al., 1985, p. 418), but of chlorites containing small amounts of biotite layers, because chlorit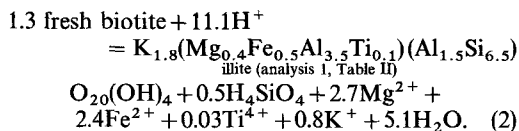es cannot accommodate K in their interlayer sites. TiO_2 in chlorite is most commonly present as finely disseminated titanium dioxide crystals and/or sphene (see, e.g. analysis 6, Table IV of White et al., 1985).

Concerning the reactions proposed by White et al. (1985) we suggest another alternative by using their 'fresh biotite' instead of the so-called 'weathered biotite' (which has very low K content). This would give a better idea of the changes which a true biotite could undergo. Moreover, chlorites containing K (and Ti) should be avoided when such reactions are constructed. By taking the above points into consideration, the formula of their chlorite was recalculated (Table I) and thus the mass-balanced reaction of fresh biotite chloritization can be presented as follows (following the style of White et al., 1985):

$$2K_2(Mg_{2.4}Fe^{2+}_{1.6})(\underset{\text{fresh biotite}}{Fe^{3+}_{0.6}Ti_{0.1}Al_{1.3}})(Al_{2.6}Si_{5.4})$$

$$O_{20}(OH)_4 + 8H_2O$$

$$= (Mg_{4.1}Fe_{4.2}Al_{3.1})(Al_{1.7}Si_{6.3})O_{20}(OH)_{16} + \underset{\text{chlorite}}{}$$

$$4.5Si^{4+} + 3.0Al^{3+} + 0.7Mg^{2+} + 0.2Fe^{2+} +$$

$$4K^+ + 8H^+ + 0.2Ti^{4+}. \quad (1)$$

The statement of White et al. (1985; p. 420) that 'relatively small changes are involved in the biotite to illite or phengite change' is not valid. Actually this biotite to illite transformation involves crystal structural changes which are kinetically more difficult than biotite to chlorite transformation. In other words, and as is well-known, the leaching of interlayer K is much easier than the almost complete rejection of octahedral Fe
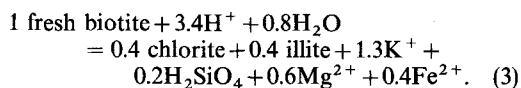
and Mg from the biotite, which results in illite as an end product. Therefore, overlooking the illitization reaction of biotite by White *et al.* (1985), who instead envisaged only biotite to chlorite reaction to be common in diagenetic and low-grade metamorphic environments, is debatable. Several authors, including White *et al.* have, however, found the biotite to illite change to occur in the environments mentioned above and also by hydrothermal alteration of biotite (see, e.g. Schwartz, 1958; Morad, 1983; Peters and Hofmann, 1984; Weaver *et al.*, 1984). Thus, such a reaction could be taken into consideration in interpreting chlorite-illite intergrowths formed from biotite. Using the chemical data presented by White *et al.* (1985), the alteration reaction of biotite to illite can be expressed as follows, if we assume conservation of Al (see, e.g. Veblen and Ferry, 1983):

$$1.3 \text{ fresh biotite} + 11.1H^+$$
$$= \underset{\text{illite (analysis 1, Table II)}}{K_{1.8}(Mg_{0.4}Fe_{0.5}Al_{3.5}Ti_{0.1})(Al_{1.5}Si_{6.5})}$$
$$O_{20}(OH)_4 + 0.5H_4SiO_4 + 2.7Mg^{2+} +$$
$$2.4Fe^{2+} + 0.03Ti^{4+} + 0.8K^+ + 5.1H_2O. \quad (2)$$

This reaction involves a molar volume reduction of about 27% in the biotite grain when completely altered into illite.

If we assume that the previous reactions account for alteration of biotite grains into mainly illite (reaction 2) or mainly chlorite (reaction 1), then the ions liberated might have been precipitated as authigenic silicates in pore spaces. These liberated ions do not necessarily form illite in a chloritized biotite (reaction 1) or chlorite in an illitized biotite (reaction 2), because in each biotite layer there is a potential source of ions which could produce both illite and chlorite separately as also suggested from microscopic observations (White *et al.*, 1985; Morad, 1986). However, if we construct a chloritization reaction of biotite by conserving Al (reaction 3; White *et al.*, 1985), then illitization of biotite layers can supply Fe, Mg, and Si ions necessary for the reaction.

Therefore, based on the conclusion that biotite accounts for intergrowths of chlorite and illite in the same grain, if Al is conserved, a net transformation reaction can be written as follows:

$$1 \text{ fresh biotite} + 3.4H^+ + 0.8H_2O$$
$$= 0.4 \text{ chlorite} + 0.4 \text{ illite} + 1.3K^+ +$$
$$0.2H_2SiO_4 + 0.6Mg^{2+} + 0.4Fe^{2+}. \quad (3)$$

The total molar volumes of chlorite and illite in reaction 3 is about 142 mole/cm³ and that of the parent biotite is about 148 mole/cm³, which means that the reduction in volume of biotite by about 4% could easily be compensated by precipitation of secondary quartz, titanium oxides and/or sphene (see e.g. Veblen and Ferry, 1983).

In summary, reaction 1, which was considered by White *et al.* (1985) to be most likely to explain the formation of chlorite-illite intergrowths, is disputable based on the following: (*a*) it does account for mass, but not charge balance, (*b*) it assumes that water (H_2O) only can produce chlorite while it is well-known that ions like H^+ are important in such reactions, (*c*) it does not involve Al^{3+} conservation and considers silica ions as Si^{4+} instead of H_4SiO_4, which is the most common form of dissolved silica used, and (*d*) it considers biotite chloritization (but ignores illitization of biotite) to be the main mechanism by which chlorite-illite intergrowths can be produced.

Variations in relative proportions of chlorite and illite revealed from microscopic examinations compared to that determined by reaction 3 above suggest that microenvironmental conditions (e.g. pH and ionic activities) of biotite alteration have exerted an important control on alteration products.

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KEYWORDS: phyllosilicates, biotites, Brøttum Formation, Norway, metamorphic rocks, sedimentary rocks.

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