Chlorites in a spectrum of igneous rocks: mineral chemistry and paragenesis

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Abstract

The chlorite data presented are from four igneous complexes covering the compositional spectrum of igneous rocks (gabbro to granite) of orogenic and anorogenic settings. The four igneous complexes are; early orogenic gabbro–diorite–tonalite (D-T) suite, late orogenic granodiorite–adamellite (G-A) suite (both are calc-alkaline suites), high-alumina trondhjemite (TR), and anorogenic peralkaline granite (PGR).

Chlorites in these igneous rocks show characteristic compositional fields. The Mg *vs* Fe plot provides the best discriminant, as data points define three compositionally different groups. Phases in the PGR are Fe-rich, siliceous, interlayered chlorite–smectite (Fe/Mg = 8.6), and differ significantly from those in the calc-alkaline D-T and G-A rocks which are Mg-rich chlorites (Fe/Mg = 0.6–0.8). The X-ray diffraction data for the peralkaline granite samples show superlattice reflections at approximately 31 Å (air-dried) and 34 Å (ethylene glycollated), thus suggesting the presence of an expandable (smectite-like) component in this interlayered (chlorite–smectite) phyllosilicate phase. Chlorites in the peraluminous TR rocks contain Fe/Mg values intermediate between the other two types (Fe/Mg = 1.3). Tetrahedral Al (AlZ) values are remarkably low (0–0.5) in phyllosilicates in the PGR, but vary from 1.9–2.5 in chlorites from the other suites. Yet, these chlorite groups with their generally low AlZ values are distinct from the more stable (type IIb) metamorphic chlorites. Sedimentary chlorites are somewhat similar, in their low AlZ values and metastable structural type, to chlorites in igneous rocks.

In the calc-alkaline rocks, chlorite may have been formed at the expense of both biotite [biotite + 3M + $3H_2O$ = chlorite + A], and calcic amphibole [2 Ca-amphibole + $6H_2O$ + $5O_2$ + 1.8Al = 1 chlorite + $8SiO_2$ + A], where M = Fe, Mg, Al, and A = K, Na, Ca. The alteration of alkali amphibole in the peralkaline rocks may have produced interlayered chlorite–smectite via this reaction; [1 Na-amphibole + $7H_2O$ + $2.5O_2$ + M = 1 chlorite–smectite + A]. The presence of such interlayered chlorite–smectite which typically form at low *T* (150–200°C) suggests that the region was not affected by any major reheating events, which is consistent with the nature of the feldspars.

KEYWORDS: chlorite, igneous rocks, alteration, Na-amphibole, smectite interlayers, paragenesis.

Introduction

INCIPIENT alteration of igneous mica and amphibole to chlorite is widespread, thus making chlorite minerals among the most abundant products of alteration in igneous rocks. Chlorites are also the principal minerals in metabasic rocks of the greenschist-and lower facies, and are common detrital and authigenic minerals in argillaceous sediments and in sandstones (Deer *et al.*, 1971; Curtis *et al.*, 1985; Bailey, 1988).

Chlorites have been extensively studied in metamorphic rocks (e.g. Weaver, 1984; Morad, 1986; AlDahan *et al.*, 1988; Laird, 1988; Bettison and Schiffman, 1988), in sedimentary rocks (Stoch and Sikora, 1976; Srodon and Eberl, 1984; Curtis *et al.*, 1985) and in geothermal systems and hydrothermal ore deposits (Innoue and Utada, 1983; Liou *et al.*, 1985; Kranidiotis and MacLean, 1987; Shikazono and Kawahata, 1987; Nutt, 1989).

Several studies have been carried out on chlorites from individual granitic plutons (Dodge, 1973; Refaat and Abdallah, 1979; Eggleton and Banfield, 1985). However, no attempt has been made to characterize chlorite minerals in the various types
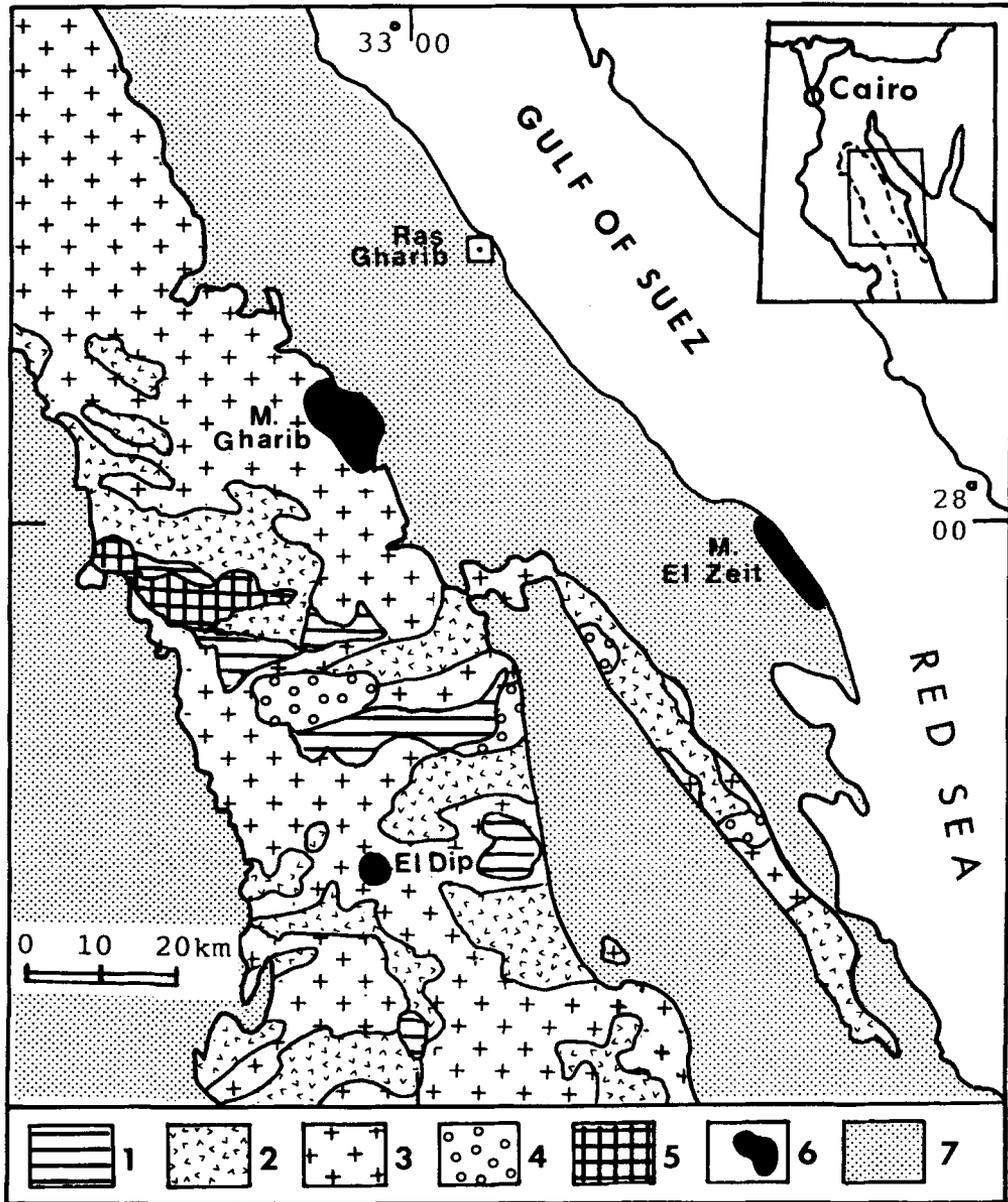
FIG. 1. Geological map of the northern part of the Nubian shield in eastern Egypt. Units: 1, diorite–tonalite (D-T); 2, 'Dokhan' volcanic rocks; 3, Pan-African granodiorite–adamellite (G-A); 4, 'Hammamat' sediments; 5, trondhjemite (TR); 6, peralkaline granites and syenites (PGR); and 7, Phanerozoic sedimentary cover. Within the location map, the area defined by dashed line represents shield rocks, and the rectangle outlines the map area.

of igneous rocks, nor to investigate the main features of these chlorites and show how they differ from metamorphic, and sedimentary chlorites. Here we present results of an investigation on chlorites occurring within four, mostly Pan-African, igneous rock suites with a wide compositional range covering the (mafic to felsic) spectrum of igneous rocks. These are the gabbro–diorite–tonalite (D-T) suite, the calc-
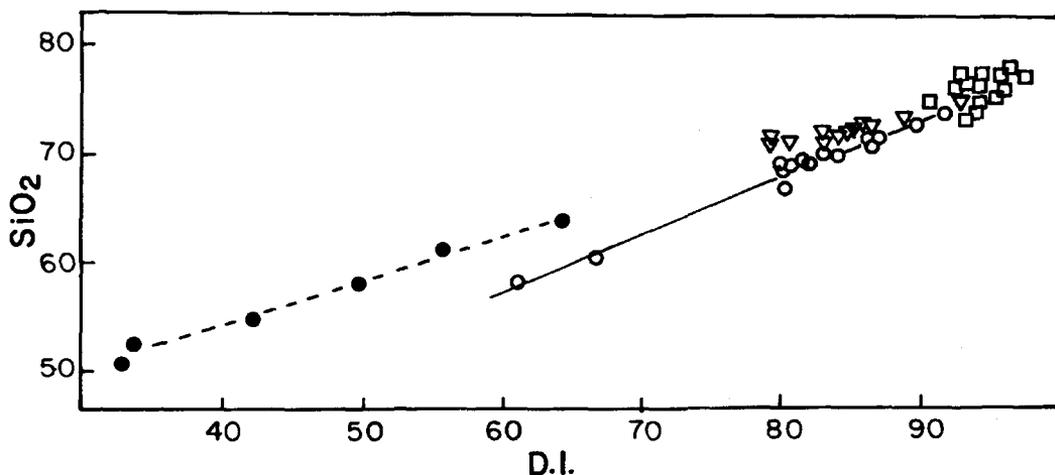
FIG. 2. Plot of SiO_2 (wt.%) vs the differentiation index (D.I., Thornton and Tuttle, 1960) for whole rock-samples: closed circles, diorite–tonalite (D-T); open circles, granodiorite–adamellite (G-A); triangles, trondhjemite (TR) and squares, peralkaline granite (PGR).

alkaline granodiorite–adamellite (G-A) suite, the peraluminous trondhjemite (TR) suite, and the peralkaline granite (PGR) complex exposed in eastern Egypt (Fig. 1). The suites were formed at various tectonic settings (see below). The aim of this contribution is to characterize these important but much overlooked phyllosilicate assemblages and document their compositional variation, isomorphism and paragenesis, in this spectrum of igneous rocks.

Geological setting

The four magmatic complexes that host the phyllosilicates (Fig. 1) are among the major crustal components of the dominantly Pan-African Nubian shield. These complexes range in age from 881 to 476 Ma (Abdel-Rahman and Doig, 1987) and, in tectonic stage, from early through late-, and post orogenic to anorogenic. Both the D-T and the G-A suites are volumetrically significant orogenic complexes.

The D-T suite includes gabbro, diorite, quartz-diorite and tonalite, forming low-lying discontinuous exposures. This suite was emplaced during the early orogenic stage, and is intruded by younger Pan-African complexes (Fig. 1). The G-A composite suite is a product of the last major shield-forming magmatic event and forms an elongate batholith which was emplaced along regional structures. This G-A composite batholith consists of a southern nonporphyritic phase that grades to the north into a porphyritic unit containing K-feldspar megacrysts.

The trondhjemite is essentially an homogeneous non-porphyritic, medium to coarse-grained, greyish white massive rock that was emplaced largely into D-T host rocks. The PGR complex is a prominent topographic feature that forms a crescent-shaped body covering an area of about 55 km^2 (Fig. 1). It was emplaced across regional structures and it intrudes two swarms of mafic to felsic dykes (some are alkaline). The PGR was emplaced during an episode of lithospheric extension caused by cooling, fracturing and relaxation of the newly formed Pan-African crust (Abdel-Rahman and Martin, 1990).

Nature of host rocks

Details of the geochemistry and petrogenesis of the igneous complexes that host the phyllosilicates are given in Abdel-Rahman and Martin (1987, 1990) and in Abdel-Rahman (1990). The main petrological-geochemical features of the complexes are outlined here to support field and mineralogical distinctions. A plot of SiO_2 vs the Differentiation Index (D.I.) after Thornton and Tuttle (1960) (Fig. 2) provides a good discriminant between the plutonic suites. The D-T suite exhibits a wide range of silica content (Fig. 2) and is geochemically primitive; it can be correlated with the so-called M-type granites, and was formed in an island-arc tectonic setting (Abdel-Rahman, 1990). The G-A suite is a typical I-type calc-alkaline orogenic suite that exhibits trace element characteristics of volcanic-arc granites; it was formed at an active continental margin (Abdel-Rahman and Martin, 1987). The TR suite belongs to

TABLE 1. Chemical composition of chlorites and the number of ions in the unit cell calculated on the basis of 28 oxygens

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	28.03	28.53	28.85	29.84	27.46	29.26	30.38	28.00	27.13	27.34	27.64
TiO_2	0.00	0.11	0.01	0.05	0.00	0.10	0.03	0.00	0.06	0.18	0.00
Al_2O_3	17.76	17.62	17.51	18.79	19.84	17.88	17.79	18.16	20.59	19.21	18.47
FeO	25.62	24.68	22.43	23.69	19.71	21.14	17.95	24.00	19.35	19.58	23.09
MnO	0.31	0.30	0.65	0.33	2.23	0.24	1.50	1.01	1.12	0.81	1.02
MgO	17.12	17.15	17.98	16.37	18.78	19.59	20.82	17.42	18.96	20.01	17.91
CaO	0.06	0.09	0.07	0.07	0.00	0.08	0.03	0.03	0.01	0.04	0.04
Na_2O	0.00	0.12	0.01	0.11	0.00	0.39	0.07	0.06	0.01	0.12	0.03
K_2O	0.04	0.07	0.00	0.01	0.00	0.03	0.03	0.02	0.01	0.34	0.01
F	0.07	0.00	0.00	0.00	0.65	0.00	0.23	0.10	0.00	0.25	0.10
$O \equiv F$	0.03	0.00	0.00	0.00	0.27	0.00	0.10	0.04	0.00	0.11	0.04
Total*	88.98	88.67	87.51	89.26	88.40	88.71	88.73	88.76	87.24	87.77	88.27
Si	5.815	5.913	5.990	6.070	5.555	5.943	6.058	5.790	5.579	5.589	5.724
AlZ	2.185	2.087	2.010	1.930	2.445	2.057	1.942	2.210	2.421	2.411	2.276
AlY	2.153	2.213	2.270	2.570	2.280	2.220	2.235	2.211	2.564	2.213	2.228
Ti	0.000	0.017	0.002	0.008	0.000	0.015	0.004	0.000	0.009	0.028	0.000
Fe	4.445	4.278	3.895	4.030	3.334	3.591	2.993	4.150	3.328	3.348	3.999
Mn	0.054	0.053	0.114	0.057	0.382	0.041	0.253	0.177	0.195	0.140	0.179
Mg	5.294	5.298	5.564	4.963	5.662	5.931	6.188	5.369	5.811	6.097	5.529
Ca	0.013	0.020	0.016	0.015	0.000	0.017	0.006	0.007	0.002	0.009	0.009
Na	0.000	0.048	0.004	0.043	0.000	0.154	0.027	0.024	0.004	0.048	0.012
K	0.011	0.019	0.000	0.003	0.000	0.008	0.008	0.005	0.003	0.089	0.003
Y	11.969	11.946	11.864	11.689	11.659	11.977	11.715	11.942	11.915	11.971	11.959
F	0.046	0.000	0.000	0.000	0.416	0.000	0.145	0.065	0.000	0.161	0.069
$\frac{Fe}{Fe+Mg}$	0.46	0.45	0.41	0.45	0.37	0.38	0.33	0.44	0.36	0.35	0.42

* Total based on measured FeO (total) values and corrected for O equivalent to F. Z and Y refer to cations in the tetrahedral and the octahedral structural sites, respectively. Phyllosilicate samples 1 to 4, from the D-T suite, 5 to 11 from the G-A suite, 12 to 16 from the TR suite, and 17 to 21 from the PGR suite.

the high-alumina trondhjemite type of Barker (1979) and is peraluminous in nature. The peralkaline granitic complex is a highly differentiated suite that is restricted to high silica values (Fig. 2), and is characterized by abundances of LIL and HFS elements typical of A-type granites (Abdel-Rahman and Martin, 1990). It was formed by partial melting of metasomatized Pan-African basement.

Petrography of the phyllosilicate's host rocks

(1) The diorite–tonalite (D-T) suite contains calcic amphibole (mostly ferroedenite; Abdel-Rahman, 1987) as the main ferromagnesian mineral, with minor augite recorded in the dioritic and gabbroic varieties. Aggregates of tabular, fine-grained brown biotite, chlorite and epidote, partially replacing large, originally poikilitic amphibole grains, are not uncommon. Individual grains of biotite and chlorite

are also present. Biotite forms 2% (by volume) whereas chlorite forms 5% of the mode, on average.

(2) The granodiorite–adamellite (G-A) suite contains variable amounts of plagioclase, K-feldspar, quartz, biotite, amphibole and chlorite. Biotite forms 1–6% of the rock (by volume), occurring as subhedral to euhedral, occasionally twinned, brown crystals with crenulated margins. Chlorite (2%) and iron oxides (magnetite) are common products of amphibole and biotite alteration.

(3) The high-alumina trondhjemite contains quartz and plagioclase with some K-feldspar, muscovite (3.5%), biotite (2.2%), chlorite (2.2%), andalusite, amphibole (confined to mafic clots), and opaque ilmenite. Euhedral muscovite occasionally inter-grown with columnar (radial) andalusite, and anhedral muscovite that occurs in sericitized plagioclase and interleaved with chlorite and biotite

Table 1, *(continued)*

	12	13	14	15	16	17	18	19	20	21
SiO_2	25.43	27.55	28.30	28.44	26.22	44.37	34.62	39.03	37.33	36.12
TiO_2	0.05	0.03	0.00	0.27	0.04	0.05	0.01	0.28	0.15	0.00
Al_2O_3	19.55	20.76	19.28	17.68	19.47	4.56	9.70	10.18	11.01	11.86
FeO	31.23	24.65	28.60	29.95	30.12	36.56	34.11	21.38	26.47	30.91
MnO	1.38	1.60	0.41	0.81	0.49	1.18	0.18	0.10	0.13	0.16
MgO	11.34	13.64	12.86	12.58	11.92	0.59	6.92	10.74	9.45	8.05
CaO	0.02	0.03	0.08	0.10	0.07	0.37	1.29	0.75	0.84	0.91
Na_2O	0.04	0.04	0.04	0.12	0.04	0.61	0.34	0.79	0.58	0.35
K_2O	0.03	0.33	0.56	0.46	0.05	0.51	0.83	4.40	2.61	0.78
F	0.00	0.05	0.00	0.00	0.03	0.00	0.28	0.06	0.04	0.00
$O \equiv F$	0.00	0.02	0.00	0.00	0.01	0.00	0.12	0.03	0.02	0.00
Total*	89.07	88.66	90.13	90.41	88.44	88.80	88.16	87.68	88.59	89.14
Si	5.487	5.732	5.887	5.963	5.624	9.509	7.542	8.094	7.804	7.604
AlZ	2.513	2.268	2.113	2.037	2.376	0.000	0.458	0.000	0.196	0.396
AlY	2.454	2.817	2.609	2.328	2.542	1.151	2.030	2.486	2.514	2.544
Ti	0.008	0.005	0.000	0.043	0.006	0.008	0.002	0.044	0.024	0.000
Fe	5.609	4.289	4.976	5.252	5.403	6.553	6.215	3.708	4.628	5.442
Mn	0.252	0.282	0.072	0.144	0.089	0.214	0.033	0.018	0.023	0.029
Mg	3.647	4.230	3.987	3.931	3.811	0.188	2.247	3.320	2.945	2.526
Ca	0.005	0.007	0.018	0.022	0.016	0.085	0.301	0.167	0.188	0.205
Na	0.017	0.016	0.016	0.049	0.017	0.253	0.144	0.318	0.235	0.143
K	0.008	0.088	0.149	0.123	0.014	0.139	0.231	1.164	0.696	0.209
Y	12.000	11.732	11.827	11.891	11.898	8.592	11.202	11.223	11.252	11.098
F	0.000	0.031	0.000	0.000	0.022	0.000	0.193	0.039	0.026	0.000
$\frac{Fe}{Fe+Mg}$	0.61	0.50	0.55	0.57	0.59	0.97	0.73	0.53	0.61	0.68

in amphibole mafic clots, are present (cf. Fig.2 of Abdel-Rahman, 1990). Large, highly pleochroic, reddish brown biotite containing numerous apatite inclusions is also present. Biotite occurs also as interstitial aggregates of small tabular grains. Large, anhedral, green chlorite grains frequently interleaved with muscovite, sericite and magnetite, replace pre-existing mafic minerals.

(4) The peralkaline granite (PGR) contains perthite, quartz and alkali amphibole (as the main mafic mineral), with minor (reddish) biotite and chlorite. Astrophyllite is more abundant than biotite in this PGR suite (Abdel-Rahman, 1992) and the opaque oxide is ilmenite. The alkali amphibole varies from ferrorichterite to end-member fluor-arfvedsonite (Abdel-Rahman, 1987). The relatively scarce biotite and chlorite in the PGR occur mostly at the expense of alkali amphibole.

Analytical techniques

Chemical analyses for chlorite minerals were obtained using polished thin sections which were vacuum-coated with C. Samples were analysed using the Cameca Camebax/microcomputer-automated electron microprobe at McGill University. The microprobe was operated using the wavelength-dispersion mode (WDS), with an accelerating voltage of 15 kV, and a beam current of $\sim$ 5 nA. With three spectrometers (LIF, PET, TAP), the procedure was most conveniently divided up by determining groups of three to five elements. Standards used for this study (e.g. ORTH, ALBI, MGO, MNTI) were McGill internal laboratory standards. The counting time was 30 s, and the standards were run for three periods.

The number of cations in the unit cell were calculated on the basis of 28 oxygens [based on chlorite formula $Y_{12}Z_8O_{20}(OH,F)_{16}$]: Y and Z represent octahedral-, and tetrahedral cations, respectively.

Sample preparation for X-ray diffraction analysis included hand-picking of phyllosilicate grains from hand samples and coarsely crushed whole rocks; a clay size fraction of the powder was used for analysis. Smear slides from suspension from bulk samples were exposed to ethylene glycol at 60°C for 24 h. The XRD analysis was performed on a Siemens

D-500 (Cu-Kα radiation with a Ni-filter) at 60 kV and 30 mA, equipped with a graphite-diffracted beam monochromator. The diffraction geometry consisted of two diffracted-beam Soller slits of 1° width each, and 1° beam- and 0.15° detector slits. Samples were step-scanned by computer control from 2–16° 2θ using a step-size of 0.01° 2θ and counting time of 1 s per step. Data aquisition was controlled by the DIFFRAC/AT software program which incorporates a DACO-MP programming card.

Results and discussion

Compositional variations of chlorite minerals. Chemical analyses of chlorites, together with the calculated unit cell formulae are presented in Table 1. The chemical composition of chlorites from the four igneous rock suites differ substantially. The Si values range from 5.45 to 6.1 cations/28 oxygens in chlorites from the orogenic suites (D-T, G-A and TR) but reach very high values (7.5–8.1) with one sample reaching 9.5 in phyllosilicates from the PGR suite.

Bettison and Schiffman (1988) showed that chlorites from the Coast Range volcanic complex, Troodos ophiolitic rocks, Onikobe and Icelandic geothermal fields that have been identified using X-ray diffraction do not have Si cation totals greater than 6.25 cations/28 oxygens, whereas those with higher values were structurally identified as various interlayered phases such as chlorite-smectite.

Samples from the orogenic calc-alkaline and peraluminous rocks (D-T, G-A and TR suites) all have Si-values less than 6.1, characteristic of chlorite, whereas those from the peralkaline PGR suite exhibit much higher Si values (7.5–9.5) and suggest chlorite–smectite interstratifications. The presence of a smectite-like component in these interlayered structures has been confirmed by X-ray diffraction (see below).

The Fe/(Fe+Mg) values in these phases vary from 0.25 to 0.5 in the D-T and G-A suites, 0.5 to 0.6 in the TR and 0.53 to 0.73 in the PGR (Table 1). The compositions of chlorite in the D-T, G-A and TR rocks fall mostly in the field of pycnochlorite, with a few samples plot in the field of ripidolite (Fig. 3), whereas samples from the PGR rocks plot in the diabantite field of Hey's (1954) chlorite classifi-caiton.

Calcium, potassium and sodium typically occur in impurities in chlorite (Albee, 1962; Deer *et al.*, 1971). Czamanske *et al.* (1981) suggested that these
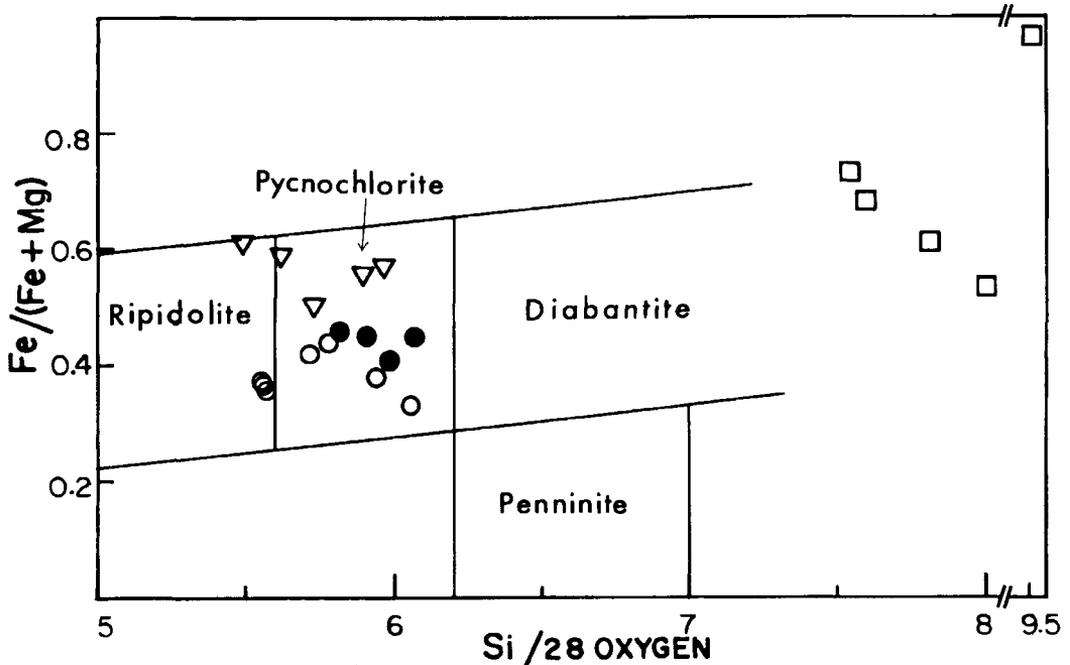
FIG. 3. Compositional variations of chlorites in terms of Fe/(Fe+Mg) *vs* Si (cations/28 oxygens). After Bettison and Schiffman (1988), modified from Hey (1954). Symbols: closed circles, chlorite from the D-T suite; open circles, chlorite from the G-A suite; triangles, chlorite from the TR suite and squares, chlorite–smectite from the PGR suite.

elements are, occasionally, absorbed or occur as interlayer cations in the chlorite. The three elements, however, occur in significantly higher contents in samples from the PGR rocks. Titanium is typically not an important constitutent of chlorite in general: Ti values vary from 0 to 0.04 in the present chlorites.

In the four igneous rock suites, Al in six-fold coordination exceeds that in four-fold coordination in most chlorites. To illustrate compositional variations in tetrahedral Al vs Fe/(Fe+Mg), Hayes (1970) and Bailey (1988) showed that over 150 chlorites from Foster (1962) and over 100 chlorites from Bailey and Brown (1962) span the complete Mg-Fe substitutional range, but occupy a narrower range in tetrahedral Al (AlZ; Fig. 4). Bailey (1988) demonstrated a broad trend of increasing AlZ with the increase in octahedral Fe within the most common structural form of chlorite (the IIb type). The latter was refined first by Steinfink (1958) and is described in Bailey and Brown (1962) and Bailey (1988).

The IIb structural type is the most stable chlorite type and occurs mostly in metamorphic rocks and in medium- to high-temperature hydrothermal ore deposits. The presence of such high-temperature chlorite in sediments was viewed by Hayes (1970) as evidence of a detrital origin. Based on X-ray diffraction and TEM studies, Hayes (1970) and Curtis et al. (1985) found that a range of authigenic sedimentary chlorites are of the Ib polytype (refined by von Engelhardt, 1942, and by Shirozu, 1955), and the so-called 'swelling chlorites' contain smectite interlayers.
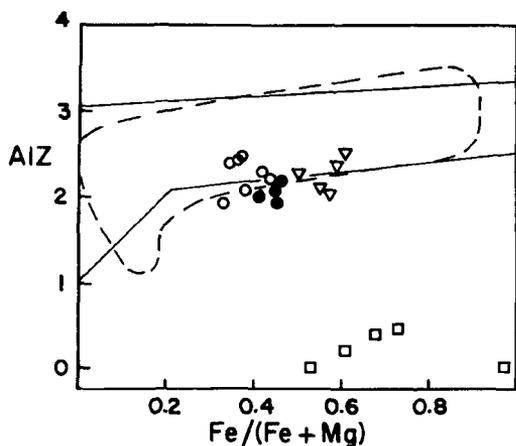
FIG. 4. Plot of Fe/(Fe+Mg) vs AlZ (Al in tetrahedral coordination) for the investigated chlorites. The field defined by a solid line is after Hayes (1970) and that defined by a dashed line is after Bailey (1988). These two fields define the compositional range of the more stable (IIb structural type) metamorphic chlorites, see text for details. Symbols as in Fig. 3.

According to Bailey (1988), the different layer-interlayer-layer sequences that are possible in the chlorite structure create varying amounts of cation–cation repulsion and cation–anion attraction as a result of the different superposition of sheets. Repulsion between the superimposed interlayer-, and tetrahedral cations in the Ia and IIa structural types reduces the stability of these two types relative to the Ib and IIb types (Bailey and Brown 1962, Shirozu and Bailey 1965).

As expected, chlorites in the investigated igneous rocks do not plot within the field of the IIb-structural type (Fig. 4), but rather near the boundary of this field that contains the range of metamorphic chlorite (defined by Hayes, 1970, and by Bailey, 1988), at lower AlZ values. The latter range from 1.9 to 2.5 for chlorites from the orogenic calc-alkaline D-T, G-A and peraluminous TR suites (Table 1; Fig. 4). This is typical of low temperature metastable chlorites formed by incipient alteration of pre-existing ferromagnesian minerals in igneous rocks (e.g. Bailey, 1988). Thus, chlorites in the investigated calc-alkaline and peraluminous rocks are similar to the sedimentary chlorites which are typically metastable structure types.

Samples from the peralkaline granites exhibit even lower AlZ values (0 to 0.5; Table 1; Fig. 4) and plot far below this field. These can be compared, in terms of AlZ values, with chlorite–smectite samples in the ophiolitic metabasalts of California (Bettison and Schiffman, 1988) and authigenic sedimentary 'swelling chlorites' described by Curtis et al. (1985).

Curtis et al. (1984, 1985) have suggested that such sedimentary swelling chlorites may be intermediate between smectite and chlorite and this would also account for their relatively higher Ca, Na and K values. It is not clear, however, what controls the presence of Ca in such phases as there is no correlation between Ca and Si, Fe, Al or Mg. In general, chlorite can accommodate only a minor amount of Ca in its structure and therefore, analyses with Ca values greater than 0.10 cations/28 oxygens indicate the presence of a smectite component (e.g. Bettison and Schiffman, 1988).

Phyllosilicates in the PGR are iron-rich siliceous phases with Ca values ranging from 0.17 to 0.30 in the unit cell (with only one sample containing 0.09, Table 1), and are thus consistent with chlorite–smectite interstratification. The X-ray diffraction patterns for samples from the PGR (Fig. 5) show superlattice reflections approximately at ~ 31 Å (air-dried) and at 34 Å (ethylene glycollated). It is obvious that the expandable component in this phyllosilicate phase corresponds to a smectite-like component that expands from 14 Å to 17 Å upon ethylene glycollation. Material having regular mixed layers between smectite and chlorite are described as

corrensite (e.g. Inoue and Utada, 1991). Thus, it is likely that the investigated interlayered chlorite–smectite may correspond to a corrensite-like structure.

A plot of Mg vs Fe (Fig. 6) provides the best discriminant between these chlorite phases. The peralkaline granites contain iron-rich interlayered chlorite–smectite (group a; Fe/Mg = 8.6, on average), whereas chlorites in the calc-alkaline orogenic D-T and G-A suites (group c; Fe/Mg = 0.8 and 0.6, respectively), are Mg-rich chlorites, and those in peraluminous rocks (the high-alumina trondhjemite, group b; Fe/Mg = 1.3) have Mg values intermediate between those two groups (a and c in Fig. 6).

The relatively smooth (negative) variation between Fe and Mg in all chlorite types, defining subparallel trends (Fig. 6), indicate a nearly one-to-one substitution between those two elements in the chlorite or chlorite–smectite structure. A similar
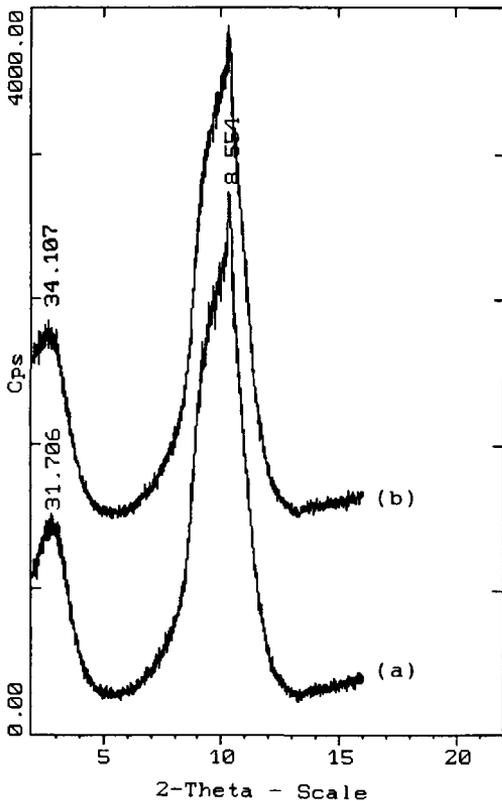
feature was observed in chlorites from the Del Puerto ophiolite (Evarts and Schiffman, 1983), the Onikobe geothermal field (Seki *et al.*, 1983), the Troodos metavolcanic rocks (Schiffman and Smith, 1988) and from the Point Sal ophiolitic metabasalt (Bettison and Schiffman, 1988).

Figure 7 shows individual compositons for chlorite–biotite, chlorite–amphibole, or chlorite–smectite and alkali amphibole pairs from the various igneous rock suites investigated. The subparallelism of tie-lines of most chlorite phases and their precursor ferromagnesian minerals indicates that the principal factor determining chlorite composition is the composition of its ferromagnesian mineral precursor (Fig. 7; see below). It should be noted that the composition of such primary ferromagnesian mineral precursors as amphibole or biotite generally reflect their host magmas. For example, Abdel-Rahman (1994) has recently documented that the composition of biotite minerals from such geochemically distinct (alkaline, calc-alkaline, and peraluminous) magma types are characteristic for each type, and clearly reflect the nature of their host magmas. The FeO/MgO ratios between whole rocks and their chlorites, when plotted, show a relatively poorer correlation, but the data still show that this ratio is preserved by the chlorites.

Chlorite paragenesis. The alteration of biotite to chlorite has been studied by several investigators including Ferry (1979), Veblen and Ferry (1983) and Eggleton and Banfield (1985). Two mechanisms for such alteration process were proposed. In mechanism

FIG. 5. X-ray diffraction patterns of samples from the peralkaline granite showing the presence of a chlorite–smectite phase with superlattice reflections at approximately 31 Å (air-dried: a), and 34 Å (ethylene glycollated: b), and alkali amphibole at 8.5 Å.
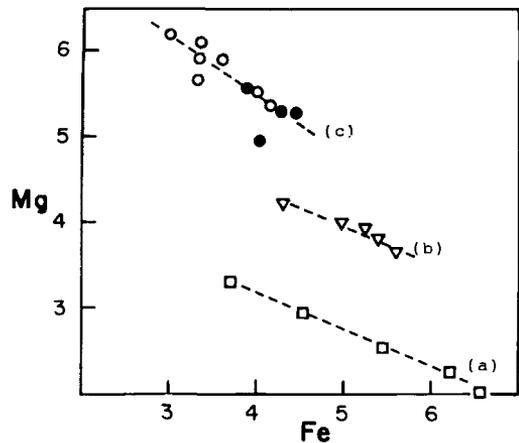
FIG. 6. Plot of Fe vs Mg (cations per unit cell). Note the negative Fe–Mg correlation and the distinct compositions of each chlorite group from the various rock suites: group a, chlorite in alkaline rocks; group b, chlorite in peraluminous rocks; group c, chlorite in calc-alkaline rocks. Symbols as in Fig. 3.

1, brucite-like layers grow into the interlayer planes (replacing the K-interlayer) of biotite to give chlorite, whereas in mechanism 2, brucite-like layers replace TOT layers (by loss of tetrahedra from these layers) to give chlorite (Veblen and Ferry, 1983). Note that a TOT layer in mica structure is composed of tetrahedral-octahedral-tetrahedral sheets. The two proposed reaction mechanisms are:

$$\text{biotite} + 3M + 3H_2O = \text{chlorite} + A \tag{1}$$

$$\text{biotite} + 10H_2O = \text{chlorite} + 4H_4SiO_4 + 2A \tag{2}$$

where M = Fe+Mg+Al+Mn and A = K+Na.

Eggleton and Banfield (1985) have proposed a reaction to produce chlorite and sericite at the expense of biotite and anorthite as follows;

$$\text{biotite} + \text{anorthite} + H_2O = \text{chlorite} + \text{muscovite} \\ + \text{titanite} + \text{epidote} + \text{quartz} + \text{magnetite} + K. \tag{3}$$
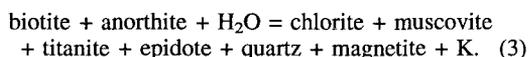
The present chlorites were produced at the expense of biotite, calcic amphibole and alkali amphibole, as observed petrographically. The composition of these amphiboles (taken from Abdel-Rahman, 1987) and of the chlorites (Table 1) have been used to write the generalized alteration reactions (4 and 5) given below. Hydrothermal alteration of calcic amphibole may have produced chlorite via this reaction:

$$2\text{Ca-amphibole} + 6H_2O + 5O_2 + 1.8Al \\ = 1 \text{ chlorite} + 8SiO_2 + A$$

$$2[(K_{0.2}Na_{0.3})(Na_{0.2}Ca_{1.8})(Mg_{2.7}Fe_{2.1}Al_{0.2})- \\ (Si_7Al_1)O_{22}(OH)_2] + 6H_2O + 5O_2 + 1.8Al \\ = 1[(Mg_{5.4}Fe_{4.2}Al_{2.2})(Si_6Al_2)O_{20}(OH)_{16}] + 8SiO_2 \\ + 0.4K + Na + 3.6Ca \tag{4}$$
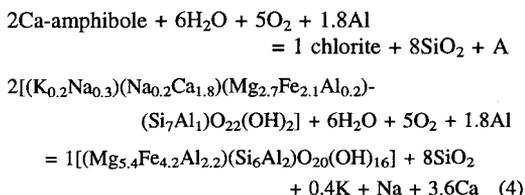
In the peralkaline granites, chlorite–smectite may have been formed at the expense of alkali amphibole
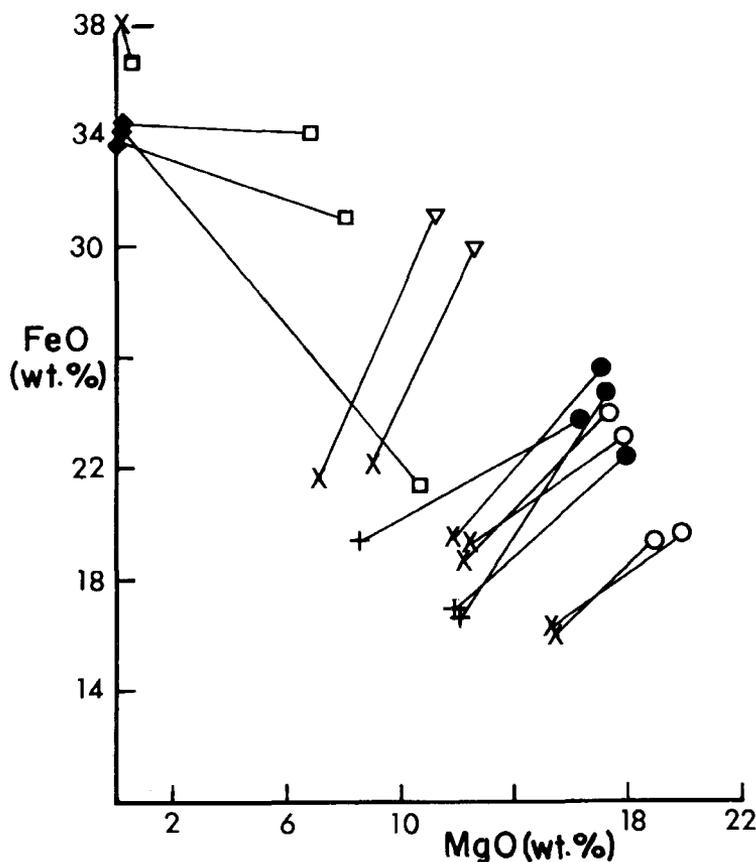
FIG. 7. Plot of FeO v. MgO (wt.%) showing the relationship between the chlorites and their precursor ferromagnesian minerals; biotite (x), calcic amphibole (+) or alkali amphibole (closed diamond). Other symbols as in Fig. 3.

as follows:

1 Na-amphibole + $7H_2O$ + $2.5O_2$ + M
$$= 1 \text{ chlorite–smectite} + A$$

$$1[(K_{0.2}Na_{0.7})(Na_1Ca_1)(Fe_{4.6}Mg_{0.4})(Si_{7.5}Al_{0.5})O_{22}(OH_{1.5}F_{0.5})]$$
$$+ 7H_2O + 2.5O_2 + 2Al + 1.8Mg + 1.6Fe$$
$$= 1[(K_{0.2}Na_{0.1}Ca_{0.3}Mg_{2.2}Fe_{6.2}Al_2)(Si_{7.5}Al_{0.5})O_{20^-}$$
$$(OH_{15.5}F_{0.5})] + 1.6Na + 0.7Ca \qquad (5)$$
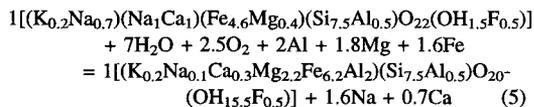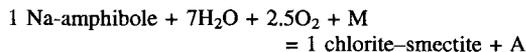
It should be noted that the alteration of one alkali amphibole produces one chlorite–smectite with the same number of tetrahedral cations (Si and Al) in the unit cell (equation 5). This may suggest that only minor adjustment in the tetrahedral layers (which may need less energy) is required for such a transformation, compared with the alteration of calcic-amphibole where two Ca-amphiboles give one chlorite, with different proportions of tetrahedral Si and Al (equation 4). The relatively lower temperature of formation of interlayered chlorite–smectite (see below), compared with the formation of chlorite that occurs at a slightly higher temperature, as recorded by Kristmannsdottir (1975, 1979) is consistent with the proposed schemes of alteration. Detailed HRTEM studies, like those carried out to characterize biotite–chlorite alteration, are necessary to document the nature of such alteration processes in both Ca- and Na-amphiboles.

Factors controlling chlorite composition. The unusually low tetrahedral Al values measured in the chlorite–smectite within the peralkaline granites and produced in equation 5 by the alteration of alkali amphibole in these rocks, demonstrates the dependency of chlorite composition on the nature of parent material which is alkali-rich and Al-poor. Also, the Fe and Mg similarities between chlorite–smectite or chlorite and their parent minerals (Fig. 7; equations 4 and 5) demonstrates the dependency of their composition on the nature of their precursor ferromagnesian minerals.

In view of the data presented here, I suggest that such interlayered Si-rich chlorite–smectite, rather than chlorite, could be the characteristic phyllosilicate alteration product in alkaline rocks in general. This could also be expected if the parent material is mica rather than alkali amphibole, since the composition of mica in most alkaline rocks is commonly Fe-rich siliceous biotite (near annite composition) with relatively low Al-contents (e.g. Lalonde and Martin, 1983; Schneiderman, 1991; Abdel-Rahman, 1994). On the other hand, the common product of the alteration of biotite and calcic-amphibole in calc-alkaline rocks is generally chlorite (equations 1 to 4).

Influence of alteration conditions. The conditions of alteration are perhaps as significant as the composition

of the starting material in controlling the nature of the phyllosilicate alteration products. Alteration conditions such as temperature, composition, and redox state of the aqueous solutions, could result in radical modifications of the products of alteration. For example, higher oxidation conditions during alteration can easily reduce the iron content of the products of alteration, thus causing major modifications of the Fe/Mg ratios of the latter. It is difficult, however, to assess the exact conditions of alteration (in such open systems) that led to the formation of the investigated phyllosilicates in the various igneous suites.

The correlation obtained between the FeO and MgO composition of the starting material and their products of alteration as shown in Fig. 7, suggests that the conditions of alteration of the various igneous rock types investigated were perhaps somewhat similar. Thus, the alteration conditions did not seem to have caused radical compositional modifications to the phyllosilicates produced. This may also suggest that the nature of the phyllosilicates presented here were largely controlled by the composition of their precursors.

Other factors controlling phyllosilicate mineral formation have been discussed by several investigators; some documented that their formation is temperature dependent. For example, Cathelineau and Nieva (1985) found that octahedral iron (FeY) and tetrahedral aluminium (AlZ) in chlorite, correlate positively with temperature. These authors have used the AlZ contents of chlorites to measure temperatures of a suite of hydrothermal chlorites from the Los Azufres geothermal area of Mexico, and have constructed a chlorite solid-solution geothermometer. A recent review of the calibrated geothermometers and geobarometers involving chlorites in metamorphic rocks is given in Laird (1988).

Keith *et al.* (1984) found the transition from smectite to mixed layered chlorite–smectite to occur at approximately 150°C at the Newberry volcano in Oregon. Kristmannsdottir (1975, 1979) has recorded the presence of mixed layered chlorite–smectite at temperatures of less than 200°C and its transition to discrete chlorite occurs in the range 200–240°C in Icelandic geothermal fields. However, Velde (1977) has shown experimentally that both chlorite and interlayered chlorite–smectite form at similar temperature and the latter interstratified phase may be controlled by the Al^{3+} (or Fe^{3+}) content of the assemblage. Lower Al contents in alkaline rocks, possibly aided by low temperature hydrothermal fluids, favour the formation of such interstratified Si-rich chlorite–smectite.

Kranidiotis and MacLean (1987) and AlDahan *et al.* (1988), among others, showed that chlorite composition in metamorphic and hydrothermally altered rocks is partly controlled by the chemistry

of the fluid phase during chlorite formation. In general, both the conditions, and fluid composition during its formation, as well as its parent material, control chlorite composition. This work demonstrates that various compositions of parent materials (biotite and amphibole) produced a variety of chlorite minerals of characteristic compositions. Since the composition of the parent material (biotite or amphibole) reflects the physiochemical conditions and composition of the silicate melt from which they have crystallized (e.g. Abdel-Rahman, 1994), chlorite compositions may reflect igneous rock types of various sources and petrogenetic histories, in a region presumably affected by similar conditions during chlorite formation.

The PGR complex that contains chlorite–smectite is the last major manifestation of igneous activity in the northern Nubian shield (Abdel-Rahman and Doig, 1987). Thus, no thermal disturbances or reheating events required to transform interlayered chlorite–smectite to chlorite post dated this complex. This is consistent with the structural state of the feldspars in the PGR (low albite and ordered microcline), determined by Abdel-Rahman and Martin (1990).

Summary and conclusions

This contribution reports on the compositions, polytypes, and possible formation reactions of chlorites from a range of igneous rock compositions. The data demonstrate that, while the alteration of calcic amphibole in igneous rocks produces chlorite (equation 4), the alteration of alkali amphibole gives interlayered chlorite–smectite (equation 5). The question of whether this is the typical alteration pattern in the calc-alkaline and alkaline igneous rocks, in general, remains to be answered via further studies of phyllosilicates in these rock types.

In view of the data presented above, it is clear that chlorites occurring in these igneous rocks are chemically distinct and define three compositionally different groups; phases in the anorogenic 'peralkaline' granitic rocks are Fe-rich, siliceous, interlayered chlorite–smectite, and differ significantly from those in 'calc-alkaline' orogenic (D-T and G-A) rocks which are relatively Mg-rich chlorites. The X-ray diffraction data for the peralkaline granite samples show superlattice reflections at ~ 31 Å (air-dried) and at 34 Å (ethylene glycollated; Fig. 5), thus suggesting the presence of an expandable (smectite-like) component in this interlayered (chlorite–smectite) phyllosilicate phase. Chlorites in the 'peraluminous' TR rocks are also chlorites, but exhibit intermediate compositions between the other two types (cf. Figs. 4, 5, 6).

Yet, these chlorite groups with their relatively low AlZ values are distinct from the more stable metamorphic chlorites (cf. Fig. 4). Sedimentary chlorites are somewhat similar, in their low AlZ values and metastable structure type, to chlorites in igneous rocks. Like the feldspars, chlorites in igneous rocks could also be used to detect reheating events and reveal the thermal history of crystalline terrains.

Compositional variations in metamorphic-, and sedimentary chlorites have been extensively characterized by a number of authors, but this is the first attempt to characterize chlorites in a spectrum of igneous rocks with distinct (peralkaline, calc-alkaline, and peraluminous) compositions. Further investigations are necessary in view of the potential for increased insight into the nature of alteration products and alteration patterns of ferromagnesian silicates in igneous rocks.

Acknowledgements

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