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H.M. Rajesh^{a,*}, O.G. Safonov^{b,c,d}, G.A. Belyanin^d, K.P. Letshele^e, C. Vorster^d

^a Department of Geology, University of Kerala, Kariavattom Campus, Bharat, India

^b Korzhinskii Institute of Experimental Mineralogy RAS, Chernogolovka, Russia

^c Department of Petrology and Volcanology, Geological Faculty, Moscow State University, Russia

^d Department of Geology, University of Johannesburg, South Africa

^e Department of Earth and Environmental Sciences, BIUST, Botswana

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ABSTRACT

Alkali metasomatism is a common overprint in Archean medium- to high-grade metamorphic terranes. Since mafic-intermediate rocks are able to host ore mineralization, it is important to understand the effect of metasomatism on its distribution. This study presents field, petrographic, mineralogical, geochemical, and U-Pb/⁴⁰Ar-³⁹Ar geochronologic characteristics of metasomatized amphibolite, amphibole gneiss and gabbro along a regional E-W section of the southeastern Motloutse Complex in eastern Botswana. The progressive metasomatism accompanies shear deformation and is visually manifested by varying degrees of pinkish discoloration of the host rocks. The metasomatic reactions in amphibolite, amphibole gneiss and gabbro are manifested in replacement of amphibole, clinopyroxene, ilmenite and plagioclase by the assemblages of chlorite, epidote, titanite, magnetite, sericite, albite and K-feldspar, up to near complete albitization and K-feldspathization with few relics of earlier minerals. Mineral compositions reflect the effects of a progressive metasomatic overprint. The metasomatic overprint resulted in the break down and dispersal of primary Cu-Ni sulphides. The pseudosection modelling (PERPLE_X) in terms of lg(aK2O) and lg(aH2O) parameters for representative compositions of leucocratic and melanocratic amphibolites, amphibole gneiss and gabbro indicates that the metasomatic process involved an increase of potassium activity followed by hydration. The modelling explains variable extent of metasomatism in different rock types. Whole-rock compositional variations indicate a general enrichment in Na_2O , K_2O and SiO_2 , and depletion in FeO and MgO in rocks during the metasomatism. ${}^{40}Ar/{}^{39}Ar$ amphibole and U-Pb titanite geochronology from metasomatized amphibolite and gabbro gave comparable ages of c.2.01-1.96 Ga. Alkaline fluids producing metasomatism were likely of crustal origin and moved along the reactivated regional c.2.01-1.95 Ga shear zones at the boundaries of the Motloutse-Limpopo complexes with the adjacent Zimbabwe and Kaapvaal cratons. Implications for a Paleoproterozoic Large Alkali Metasomatic Province (LAMP) in southern Africa, and its relation to the Bushveld large igneous province (LIP) is explored.

1. Introduction

Archean amphibolite- to granulite-facies metamorphic terranes usually show extensive reworking due to post-peak deformational, thermal, anatectic and metasomatic events. The metasomatic overprint events accompanying shear deformation are usually the last ones. Outcrop- to regional-scale albitization of granitoid gneisses is a widely reported example of such late metasomatism (e.g., Oliver et al., 1994; Engvik et al., 2008; Kaur et al., 2014). In comparison to granitoids, mafic-intermediate rocks in Archean medium–high-grade metamorphic terranes are less studied in terms of effect of metasomatism on them. Since the mafic-intermediate rocks are common host for Cu-Ni sulphide mineralization (Naldrett, 2004; Ernst, 2014; Smith and Maier, 2021), it is important to evaluate the role of metasomatism on redistribution and

* Corresponding author. *E-mail address:* rajesh.hm@gmail.com (H.M. Rajesh).

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accumulation of ore components. Metasomatic fluids could both assist the transport of ore components and their concentration into mineral deposits, and result in the breakdown of ore minerals and dispersal of ore components.

The present study characterizes the effect of alkali metasomatism on amphibolite, amphibole gneiss and gabbro from the Motloutse Complex terrane in eastern Botswana. Field, petrographic, mineral chemical and whole-rock geochemical data of samples from a regional E-W section evaluates the nature and extent of metasomatism, as well as its effect on the host rocks. Phase equilibria modelling is applied to describe the metasomatic process in terms of K₂O and H₂O activities. A combination of ⁴⁰Ar/³⁹Ar geochronology on amphibole and U-Pb geochronology on titanite provide time constraints. The results have implications for ore exploration of mafic-intermediate rocks in Archean medium–high-grade metamorphic terranes, and delineating a large alkali metasomatic province in southern Africa.

2. Geologic setting

The present study concerns the medium- and high-grade metamorphic terranes of the Motloutse and Limpopo complexes situated between the Zimbabwe and Kaapvaal cratons in southern Africa (Fig. 1a, b). The focus is on southeastern Motloutse Complex, with extrapolation of results to a regional context covering the nearby Limpopo Complex.

2.1. Limpopo complex

The Limpopo Complex is a collage of Paleoarchean to Paleoproterozoic high-grade metamorphic terranes between the Zimbabwe and

Kaapvaal cratons (Fig. 1a, b). It is primarily divided into the Northern Marginal Zone to the SE of the Zimbabwe Craton, the Southern Marginal Zone to the NE of the Kaapvaal Craton and the Central Zone between the two marginal zones (Fig. 1a, b; reviews in Blenkinsop, 2011; Smit et al., 2011; Van Reenen et al., 2011). The Central Zone is further subdivided into the Beit Bridge Complex, Phikwe Complex and the Mahalapye Complex (Fig. 1a, b; Aldiss, 1991). The different zones are separated from each other and adjacent cratons by the North Limpopo Thrust Zone, Triangle Shear Zone, Palala-Tshipise shear zones, and the Hout River Shear Zone (Fig. 1a, b; McCourt and Vearncombe, 1992; Smit et al., 1992; Blenkinsop et al., 1995). Both the marginal zones are dominated by pyroxene-bearing granitoid gneisses (charnockites) with less dominant meta-mafic, -ultramafic and -sedimentary lithologies, and are respectively thrust on to the adjacent cratonic domains (reviews in Blenkinsop, 2011: Van Reenen et al., 2011). In comparison, continental shelf type meta-supracrustal rocks and granitoid gneisses are dominant rocks in the Central Zone. Among the granitoid gneisses, Paleoarchean rocks occur in the Beit Bridge Complex, Neoarchean ones comprise both the Beit Bridge and Phikwe complexes, while mappable units of the Paleoproterozoic rocks are restricted to the Mahalapye Complex (reviews in Smit et al., 2011). Prominent episodes of Neoarchean granulite-facies metamorphism and localized Paleoproterozoic metamorphism are reported from the different terranes (reviews in Rigby et al., 2008; Blenkinsop, 2011; Smit et al., 2011; Van Reenen et al., 2011; Brandt et al., 2018).

2.2. Motloutse complex

The Motloutse Complex in eastern Botswana is an Archean



Fig. 1. Generalized outline map (a) and geologic map (b) of the known extents of the medium–high-grade metamorphic terranes and sub-terranes of the Limpopo and Motloutse complexes and adjacent regions of the Zimbabwe and Kaapvaal cratons in southern Africa [modified from Watkeys (1983), Aldiss (1991), Rajesh et al., (2022a)]. The present study focuses on a E-W transect [red horizontally elongate rectangle in (b)] in southeastern Motloutse Complex. The vertically elongate orange rectangle covers the extent of area covered in Fig. 2a, b. sz – shear zone; Dsz – Dikalate Shear Zone; Msz – Magogaphate Shear Zone; Grp – Group; SupGrp – Supergroup. Inset in (b) is a satellite image of southern Africa showing the known extents of Zimbabwe and Kaapvaal cratons. The orange rectangle indicate the approximate extent of the area covered in the main map.

allochthonous terrane at the southwestern margin of the Zimbabwe Craton and to the west of the Limpopo Complex (Fig. 1a, b; Aldiss, 1991; Carney et al., 1994; McCourt et al., 2004; Rajesh et al., 2024). The northern margin of the Motloutse Complex is thrust northeastwards on to the Zimbabwe Craton margin along the SW-dipping Shashe Shear Zone (Fig. 1a, b; Aldiss, 1991; Carney et al., 1994; Paya et al., 1997; McCourt et al., 2004). The ENE-WSW-trending Magogaphate and N-S trending Dikalate shear zones separate the Motloutse Complex from the Phikwe Complex to the east (Fig. 1a, b; Aldiss, 1991; Key et al., 1994; Paya et al., 1997; McCourt et al., 2004). To the southwest, the Motloutse Complex is faulted against cover rocks of the Palapye Group and Karoo Supergroup but is interpreted to extend under cover as far as the Mahalapye Complex (Fig. 1a, b; NW-SE trending Sunnyside Shear Zone; Rajesh et al., 2022a). The western margin of the Motloutse Complex is obscured under cover rocks.

The Motloutse Complex consists of c.3.02–2.82 Ga mafic–ultramafic rocks, c.2.71-2.63 Ga granitoid gneisses, and c.2.66-2.64 Ga metasedimentary rocks (Fig. 1b; Aldiss, 1991; Carney et al., 1994; Key et al., 1994; Holzer et al., 1999; McCourt et al., 2004; Zeh et al., 2009; Rajesh et al., 2020a). The Mesoarchean mafic-ultramafic rocks of the Lechana layered complex and massive amphibolite in the southeastern part of the terrane occur as inclusions within the granitoid gneisses (Rajesh et al., 2020a, 2022b). The Neoarchean granitoid varieties include tonalitic gneisses, migmatitic granodioritic to granitic gneisses, and porphyritic granites (Key, 1976; Smith and Phofuetsile, 1985; Aldiss, 1989, 1991; Carney et al., 1994; Key et al., 1994). The Neoarchean Shashe Group of metasedimentary rocks in the northern-central parts of the terrane include quartzites, quartz-mica schists, marbles, calc-silicates, with minor pelites and ironstones (Fig. 1b; Key, 1976; Smith and Phofuetsile, 1985; Aldiss, 1989, 1991; Key et al., 1994). Metamorphic conditions in the Motloutse Complex vary from lower greenschist-facies in the metasedimentary rocks to amphibolite-facies in the metabasic rocks (Key, 1976; Aldiss, 1989, 1991; Smith and Phofuetsile, 1985; Key et al., 1994; Holzer et al., 1999; Buick et al., 2007). A localized Paleoproterozoic overprint involving concomitant anatexis, shear deformation, and alkali metasomatism is reported from the southeastern part of the Motloutse Complex (Rajesh et al., 2020a). Basupi et al. (2022) reported temperatures of 850-910 °C for the Paleoproterozoic anatectic overprint. In comparison to the adjacent Limpopo Complex, no evidence for Neoarchean granulite-facies metamorphism and charnockites are reported from the Motloutse Complex.

3. Amphibolite-hosted Selebi-Phikwe sulphide deposit

The Selebi-Phikwe Ni-Cu sulphide deposit in eastern Botswana is part of the high-grade Phikwe Complex (Fig. 1a, b). Massive and disseminated sulphides primarily occur in amphibolite sequences with or without associated minor peridotite and pyroxenite, and are surrounded by granitoid gneisses [supplementary online material Fig. DR1; Gordon, 1973; Key, 1976; Wakefield, 1976; Marsh, 1978; Lear, 1979; Brown, 1988; Maier et al., 2008]. In comparison to amphibolite, the ultramafic rocks are weakly mineralized with sulphides. The amphibolite sequences comprise massive amphibole-rich mafic* amphibolite and feldspathic* amphibolite, with varying proportion of amphibole and plagioclase [Fig. DR1; *nomenclature following Brown (1988)]. Both types of rocks could be variants of the same rock unit or separate units. Field relations indicate gradation from amphibole-rich rock to a plagioclase-dominant one (Fig. DR1; Brown, 1988). Garnet prominently occurs adjacent to the massive sulphide layers in amphibole-rich mafic amphibolite (Fig. DR1). There is remobilization of sulphide into the garnet porphyroclasts. The content of disseminated sulphide decreases to the plagioclase-dominant rock (Fig. DR1; Brown, 1988). The protolith of the amphibolite sequences are tholeiitic basalts (Brown, 1988; Maier et al., 2008). They could be either volcanic flows and/or sill-like intrusions, which now occur as dismembered units within granitoid gneisses (Gordon, 1973; Wakefield, 1976; Marsh, 1978; Lear, 1979;

Brown, 1988). In view of the intrusive field relation of the granitoid gneisses with the amphibolites, the latter are older than c.2.65–2.61 Ga (Wakefield, 1976; Brown, 1988; McCourt and Armstrong, 1998; Holzer et al., 1999; Chavagnac et al., 2001; Zeh et al., 2009). There is evidence for granulite-facies metamorphic overprint in the mafic rocks (Lear, 1971; Brown, 1988; Key et al., 1976; Aldiss, 1983), and could be related to c.2.61 Ga and/or c.2.04 Ga high-grade event in the Phikwe Complex (Hickman and Wakefield, 1975; Holzer et al., 1999; Zeh, 2008 unpublished U-Pb monazite age quoted in Millonig, 2009; Zeh et al., 2009). Despite varying degree of hydrothermal alteration, no prominent alkali metasomatic overprint is reported from the host rocks of the Selebi-Phikwe sulphide deposit.

The Bamangwato Concessions Limited, which mined the Selebi-Phikwe sulphide deposit, carried out regional soil sampling program in southeastern Motloutse Complex (Lindsay et al., 1969; Rawle, 1969), the region to which the present study area belongs. Although high Ni + Cr \pm Cu anomalies were reported (Lindsay et al., 1969; Rawle, 1969), detailed exploration is yet to be conducted. In view of the similarity of rock types between the Selebi-Phikwe region and southeastern Motloutse Complex, the results presented here could be of use for future exploration activities.

4. Methodology

Field mapping of the study area in southeastern Motloutse Complex was supplemented with aeromagnetic data derived maps. Various analytical methods were employed on representative rock samples collected from the study area. After detailed petrography study using transmitted-light, reflected-light and back-scattered (BSE) imaging, mineral chemical analyses were obtained using electron microprobe analyser (EPMA). Bulk rock major, trace and rare earth element contents were respectively obtained using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS). To clarify time constraints, ⁴⁰Ar/³⁹Ar amphibole and U-Pb titanite geochronology data were respectively obtained using noble gas spectrometry and laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS). Finally, phase equilibria modelling using the PERPLE_X software (Connolly, 2005) was carried out to evaluate the progress of metasomatism. Details of the different methods employed in the study are given in supplementary online material Fig. DR2.

5. Results

5.1. Field relations of the Masikate-Maope section, southeastern Motloutse Complex

The present study focuses on an E-W section of the southeastern Motloutse Complex between the N-S trending Dikalate Shear Zone along the Masikate Hill, and its branches, up to the Maope Hills (Fig. 1 and 2a–d). In addition, the study concerns rock types exposed at the Maope quarry located in the west of the study area (Fig. 2c). Various rock types are well exposed along the hills and ridges (Fig. 2c), but exposure in the surrounding low-lying areas is poor (Fig. 2c).

The major rock types in the study area are tonalite gneiss, amphibolite, gabbro-leucogabbro-anorthosite sequences, and peridotitepyroxenite sequences (Fig. 2c, d and supplementary online material DR3). The dominant 2645 ± 22 Ma (U-Pb zircon; Zeh et al., 2009) tonalite gneiss occupy the low- and high-lands, whereas the mafic–ultramafic rocks dominate the hills and ridges (Fig. 2c, d). Xe-noliths of mafic–ultramafic rocks in tonalite gneiss indicate that they are older than the felsic rock (Figs. DR3a, b). The gabbro-leucogabbro-anorthosite and peridotite-pyroxenite sequences form part of the c.2817–3020 Ma (U-Pb zircon) Lechana layered complex (Figs. DR3c–f; Rajesh et al., 2020a, 2022b). Magmatic field relations of the mafic and ultramafic layered sequences are variably preserved in the hills and ridges. No geochronologic data is available on the spatially associated



Fig. 2. Aeromagnetic data derived maps of southeastern Motloutse Complex showing the extent of the Dikalate Shear Zone (Dsz) and its branches. (a) Reduction to magnetic pole (RTP) map; (b) Greyscale first vertical derivative (1VD) map. The different geologic features indicated include the NW-SE trending Lechana Fault, ENE-WSW trending Magogaphate Shear Zone (Msz), N-S trending Dikalate Shear Zone (Dsz), and the WNW-ESE trending mafic dykes (linear high magnetic bodies in 2a). The large magnetic body (reddish to pinkish) that occurs around Dikalate and extends up to the east of Masikate in 2a is a porphyritic alkali granite pluton with xenoliths of tonalite gneiss and amphibolite. See DR2 for details of aeromagnetic image analyses. The white rectangle indicate the extent of area covered in (c) and (d). Landsat 8 satellite image (c) and geologic map (d) of the study area from southeastern Motloutse Complex. The mapped extent of the N-S trending Dikalate Shear Zone along the Masikate Hill and its branches are shown in (b). Approximate location of samples (stars) for geochronology in this study and Rajesh et al., (2020a), respective ages and geochronology methods (in parentheses) are indicated in (c).

amphibolite. But the intrusive field relation, including the presence of amphibolite enclaves in the mafic–ultramafic rocks, argue for a contemporaneous, but slightly older age (>3.02 Ga) for the amphibolite (Rajesh et al., 2020a). Concomitant anatexis, shear deformation and metasomatism variably overprint the different rock types in the study area. The anatectic overprint is dated between 2056 ± 12 Ma (anatectic leucocratic vein-bearing tonalite gneiss; U-Pb zircon overgrowth; Zeh et al., 2009), and 2020 ± 5 Ma (garnet-bearing amphibolite; U-Pb zircon overgrowth; Basupi et al., 2022). The shear deformation is related to the N-S trending Dikalate Shear Zone (Dsz), and its branches (Fig. 2a–d). A U-Pb zircon overgrowth age of 2013 ± 8 Ma dates the shear deformation (Fig. 2c, d; Rajesh et al., 2020a). Metasomatic overprint is associated with the shear deformation. However, no geochronologic data is available on it.

A set of NW-SE trending, undeformed, dolerite dykes cut across all other rock types (Fig. 2a–d). The dykes are mostly not exposed (except across the Masikate Hill; Fig. 2c, d), but are discernible in aeromagnetic

images (Fig. 2a, b). Taking into account the similarity of trend to the Okavango dyke swarm in eastern Botswana (Carney et al., 1994; Le Gall et al., 2002), the NW-SE dykes likely belong to the Phanerozoic Karoo Group.

Rocks in the Masikate-Maope areas show variable degree of pinkish discoloration manifesting alkali metasomatism. The degree of metasomatism generally increases towards the Dikalate Shear Zone and its branches. The effect of metasomatism on the tonalite gneiss is presented first, followed by that of amphibolite, gabbro and amphibole gneiss; the later rock type is newly reported in this study. Ultramafic rocks, which do not exhibit any visible effect of alkali metasomatism, are not considered in this study.

5.1.1. Tonalite gneiss

The banded greyish biotite-bearing tonalite gneiss show tight folds with well-developed limbs (supplementary online material Figs. DR4a, b). The anatectic overprint is manifested by irregular leucocratic domains and boudin structures concordant to the gneissic fabric, as well as by the local presence of garnet (Figs. DR4a, c). No anatectic domains discordant to the deformation features were observed. Both the tight folds and anatectic veins are offset by pervasive shear deformation, expressed in a reorientation of the gneissic banding into cm-scale shear zones (Figs. DR4d–f). A dominant right with minor left lateral sense of movement is inferred for the shear deformation (Figs. DR4d–f).

The shear deformation is accompanied by pervasive alkali metasomatic overprint. It grades from pinkish discoloration along gneissic layering, tight folds, anatectic veins-boudins and shear planes in the less metasomatized greyish gneiss (Figs. DR4a–f) through large pinkish domains with greyish gneissic relics (Fig. DR4g) to the near complete replacement of the gneiss by the deep pinkish rocks (Fig. DR4h). Veins of yellowish-green to greenish epidote commonly fill fractures within the metasomatized tonalite gneiss. The contact zone between the tonalite gneiss and amphibolite serve as a potential site of extensive metasomatism (Fig. 3a). The contact between the pinkish and greyish (host rock) domains is in general gradational.

5.1.2. Amphibolite-gabbro

The next dominant rock in the study area is amphibolite, which occur as xenoliths of variable size in the tonalite gneiss (Fig. 2d and DR3a, b). Amphibolites are massive melanocratic (amphibole-rich) or leucocratic (plagioclase-dominant) gneissic rocks, with a sharp contact between the two rock types (Fig. 3b). Enclaves of the dark amphibole-rich rock locally occur within the greyish plagioclase-dominant one. Amphibolite is closely associated with gabbro-leucogabbro-anorthosite (Fig. 2d), and occurs as enclaves within the individual gabbroic rocks. Like in the tonalite gneiss, tight folds and boudin structures deform the planar fabric in the amphibolite. An anatectic overprint in the amphibolite and gabbro is manifested by irregular garnet-bearing leucocratic veins that are concordant to the host rock fabric. The size of garnet in amphibolite reaches up to 5 cm. The effect of shear deformation in amphibolite and gabbro is expressed by asymmetric folded veins, porphyroclasts and high strain zones. Pervasive alkali metasomatism accompanying shear deformation is expressed in the pinkish discoloration along pathways defined by earlier structures in the amphibolite (Fig. 3c-e). In comparison to the melanocratic amphibolite, the extent of metasomatic overprint is prominent in the leucocratic amphibolite. The contact between the pinkish and host rock domains are in general gradational. Deep pinkish discoloration characterize the most extensively metasomatized amphibolite (Fig. 3f). Deep pinkish bands with amphibolite inclusions, locally cuts across the rock, and are characterized by sharp contacts (Fig. 3g). Centimeter- to meter-scale epidote veins/bands/aggregates are commonly associated with metasomatized amphibolite (supplementary online material Fig. DR5). In contrast to tonalite gneiss and amphibolite, evidence for alkali metasomatic overprint (pinkish discoloration) is scarce in gabbro, leucogabbro and anorthosite. But, yellowish green to greenish epidote-rich veins are associated with gabbroic rocks (Fig. 3h and DR5).

5.1.3. Amphibole gneiss

Different stages of metasomatism of the above rock types are widely represented in the regional E-W section between the Masikate and Maope hills (Fig. 2c). In addition, a near continuous traverse showing the progression of metasomatism is preserved in amphibole gneiss that is exposed at the Maope quarry (location in Fig. 2c). The mesocratic amphibole gneiss with dioritic texture exhibit intrusive contact relation with amphibolite (Fig. 4a). The contact between amphibole gneiss and biotite-bearing tonalite gneiss is not exposed. But amphibolite xenoliths occur in both gneiss. The different stages of metasomatized) rock through greyish-pink and pinkish to a deep pinkish (most metasomatized) rock. The metasomatism progresses from pinkish patches through irregular and regular outlined veins to bands (Fig. 4b–e). The pinkish veins and bands form a network in the host rocks (Fig. 4f, g). The most extensively metasomatized domains show deep pinkish to (locally) reddish discoloration, and contain quartz- and epidote-rich aggregates (Fig. 4h–j).

5.2. Petrography

5.2.1. Amphibolite and amphibole gneiss

Amphibolite vary from amphibole-rich rock with minor plagioclase (Fig. 5a; melanocratic amphibolite) to a plagioclase-dominant rock (Fig. 5e; leucocratic amphibolite). The rocks show variable content of quartz, contain accessory ilmenite, apatite and zircon. Garnet (after amphibole) and associated felsic domains with irregular lobate grain margins reflect anatectic overprint. Elongated quartz, amphibole, plagioclase and garnet aligned parallel to the ductile fabric mark effect of shear deformation. They contain recrystallized quartz with or without sutured grain margins, and locally plagioclase grains with bent twin planes. The amphibole gneiss is similar in mineralogy to the amphibolite, but richer in plagioclase. These rocks show a dioritic texture (Fig. 6a).

Effects of metasomatism are considered for melanocratic amphibolite (Fig. 5a-d and supplementary online material DR6), leucocratic amphibolite (Fig. 5e-h and supplementary online material DR7), amphibole gneiss (Fig. 6a-d and supplementary online material DR8) and associated deep pinkish rock (Fig. 6e-h and supplementary online material DR9). In contrast to the amphibole-rich rock (Fig. 5a-d and DR6), the effect of metasomatism is prominent in the plagioclase-rich rocks (Fig. 5e-h, 6a-d and DR7, 8). However, the pattern and progression of metasomatism are comparable in the different rock types (Figs. 5, 6 and DR6 to 8). The original rock fabric is almost completely obliterated in the most metasomatized rocks (Fig. 6e-h and DR9). In the least metasomatized rocks, chlorite (Fig. 5a) or epidote (Fig. 6a) locally form after amphibole. In the more metasomatized rocks, amphibole is extensively replaced by chlorite and epidote either separately or by aggregates of these minerals, whereas plagioclase is replaced by sericite, albite and K-feldspar (Fig. 5b-d, 5f-h, 6b-d and DR6 to 9). Titanite usually accompanies the partially replaced amphibole, and is prominent in the amphibole gneiss (Fig. 6a and DR8). Magnetite is a common oxide phase in the more metasomatized rocks. Epidote \pm chlorite-rich veins crisscross the albite-K-feldspar-quartz dominant rocks and, locally, converge into bands (Fig. DR9). With increasing fluid pathways, metasomatized grains get broken down or elongated and dispersed (Fig. 6e, f and DR9). Albite is prominent, but K-feldspar is absent in the amphibolerich rock. In comparison, both albite and K-feldspar modal contents increase during metasomatism of the plagioclase-rich rocks. The albitization and K-feldspathization of the rock progresses to near completion with few relics of earlier minerals (Fig. 6g, h and DR9). In the garnetbearing amphibolite, the metasomatism results in fragmentation of garnet porphyroblasts into smaller grains associated with chlorite, epidote and sericite aggregates (supplementary online material Fig. DR10).

5.2.2. Gabbro

The mineral assemblage of gabbro is clinopyroxene + plagioclase with minor quartz and accessory ilmenite apatite and zircon (Fig. 7a). Brownish amphibole replaces clinopyroxene (Fig. 7a, e). The extent of metasomatism of gabbro is less compared to the amphibolite and amphibole gneiss. However, the pattern and progression of metasomatism of the rocks are comparable (Fig. 7a–d and supplementary online material DR11). In the least metasomatized gabbro, epidote locally replace clinopyroxene and amphibole along its margins (Fig. 7a). With increase in the degree of metasomatism, epidote and chlorite replace clinopyroxene-plagioclase and plagioclase-plagioclase interfaces (Fig. 7b–f and DR11). Clinopyroxene and amphibole are extensively altered, plagioclase is sericitized and albite forms locally in the more metasomatized gabbro (Fig. 7g, h). No K-feldspar occurs in the gabbro.



Fig. 3. Representative field photos illustrating the progression of pinkish discoloration related to pervasive alkali metasomatism of amphibolite (a to g) and gabbro (h) in the E-W transect shown in Fig. 2d. (a) The contact zone of greyish tonalite gneiss and amphibolite are potential sites of extensive metasomatism. (b) Amphibole-rich melanocratic amphibolite and plagioclase-dominant leucocratic amphibolite, with sharp contact between them. (c)–(e) Pinkish discoloration following earlier structures including layering, tight folds and boudin structures in amphibolite. (f) The most extensively metasomatized amphibolite is characterized by deep pinkish domains. (g) Deep pinkish bands with inclusions of amphibolite, locally cuts across the rock. (h) Yellowish-green to greenish epidote-rich domains associated with gabbroic rocks.



Fig. 4. Representative field photos characterizing the progression of metasomatism of amphibole gneiss at the Maope quarry. (a) Intrusive contact relation of amphibole gneiss and amphibolite. (b)–(e) The metasomatism in amphibole gneiss progresses from pinkish patches to irregular outlined veins to more regular outlined veins to bands. (f) The veins and bands invade the host rock and form a network. (g), (h) Quartz-rich and epidote-rich domains becomes prominent with increase in the degree of metasomatism. (h)–(j) Deep pinkish to (locally) reddish discoloration, with associated quartz- and epidote-rich domains characterize the most extensively metasomatized amphibole gneiss.



Fig. 5. Representative photomicrographs illustrating the progression of metasomatism in melanocratic (a–d) and leucocratic (e–h) amphibolite. **(a)** Melanocratic amphibolite is amphibole(Amp)-rich with minor plagioclase (Pl) in a granoblastic polygonal texture. The least metasomatized rocks can show local replacement of amphibole by chlorite (Chl). **(b)–(d)** In more metasomatized rocks, amphibole is replaced by chlorite and epidote (Ep) either separately or together as intergrowths. Albite (Ab) increases in modal content. **(e)** Leucocratic amphibolite is characterized by dominant plagioclase and less amphibole in a granoblastic polygonal texture. The least metasomatized leucocratic amphibolite can show local replacement of amphibole by epidote. **(f)–(h)** Amphibole is replaced by epidote and chlorite either separately or together as intergrowths. Albite (Ab) and K-feldspar (Kfs) increases in modal content. Qz – quartz; Ilm – ilmenite. All images taken under plane polarized light (PPL). Additional images in DR6 and 7.



Fig. 6. Representative photomicrographs illustrating the progression of metasomatism in amphibole gneiss (a–d) and associated deep pinkish rock (e–h). (a) Titanite (Ttn) grains conspicuously follow metasomatized amphibole. (b)–(d) Amphibole can be replaced by epidote and chlorite either separately or together as intergrowths. Albite and K-feldspar increases in modal content. (e), (f) With increasing fluid pathways, metasomatized grains get broken down or elongated and dispersed. (g), (h) The albitization and K-feldspathization of the rock progresses to near completion with few relics of earlier minerals. All images taken under PPL. Additional images in DR8 and 9.



Fig. 7. Representative photomicrographs (a–d) and back scattered electron (BSE) (e–h) images illustrating the progression of metasomatism and occurrence of sulphides in gabbro. (a) Least metasomatized gabbro with clinopyroxene (Cpx) and plagioclase. Amphibole occurs along the margin of clinopyroxene. Sulphides are widely distributed. Epidote locally replace clinopyroxene and amphibole along its margins (inset), and rims sulphide. (b)–(d) Pattern of progression of metasomatism in gabbro. Titanite conspicuously follow metasomatism, and typically occur at the clinopyroxene-plagioclase and plagioclase-plagioclase interfaces. (e)–(h) Sulphides occur interstitial to plagioclase or along clinopyroxene-plagioclase interface. Amphibole replacing clinopyroxene is seen in (e). Epidote and chlorite replace clinopyroxene and amphibole, being accompanied by titanite forming along the clinopyroxene-plagioclase and plagioclase-plagioclase interfaces. Epidote form conspicuous rims around sulphides (e, f). (a)–(d) taken under PPL. Additional images in DR11.

5.2.3. Sulphides

Sulphides are common in amphibolite and amphibole gneiss (Figs. 5 and 6). They are more abundant in the melanocratic amphibolite than in the leucocratic amphibolite or amphibole gneiss (Figs. 5 and 6). Sulphides in these rock types are dominantly interstitial, and locally form inclusions (Fig. 5a, b, e, f, h, 6a–d and DR10). Sulphides along the plagioclase-plagioclase and clinopyroxene-plagioclase interfaces are common in the gabbro, as well (Fig. 7a–h and DR11). The sulphide content in amphibolite and gabbro reaches up to 5 modal%, and up to 3 modal% in amphibole gneiss. In all the rocks, sulphides are represented by pyrrhotite (70–80 %), pyrite (5–15 %), chalcopyrite (5–8 %), and pentlandite (1–3 %) (Fig. 7e–h, 8a–h, 9n and supplementary online material DR12a). Locally, chalcopyrite is replaced by covellite and pyrrhotite is replaced by marcasite.

Epidote form conspicuous rims around sulphides in the metasomatized gabbro (Fig. 7e, f). With an increase in the degree of metasomatism, the margins of sulphide grains are broken down and dispersed around epidote \pm chlorite-rich domains (Fig. 8a, b). In comparison, the effect of metasomatism is prominent and widespread on sulphides in the melanocratic and leucocratic amphibolite, and amphibole gneiss; more so in plagioclase-rich rocks than the amphibole-rich one. Three patterns are observed in these rocks (Fig. 8c–h and DR12): (1) sulphide grains are broken down into smaller fragments, and carried away by chlorite \pm epidote aggregates (Fig. 8c, d and DR12b–h); (2) sulphide grain margins are dusted to smaller grains and scattered by chlorite \pm epidote aggregates (Fig. 8e, f and DR12i–p); (3) sulphide grains are thinned down parallel to chlorite \pm epidote microveins and carried away (Fig. 8g, h and DR12q–x). The breaking down, scattering and dispersal of sulphide grains increases with the extent of metasomatism.

5.3. Mineral chemistry

This section describes compositional variations of minerals from the least metasomatized to the more metasomatized rock varieties (Fig. 9a–f). The term "partly metasomatized" is applied to rocks whose degree of metasomatism is intermediate between least and more metasomatized rocks. The mineral chemical data are listed in supplementary online material Tables DRT1 to 8. In the case of amphibolite, the least metasomatized group primarily consists of analyses from the melanocratic amphibolite. On the other hand, analyses from the leucocratic amphibolite and amphibole gneiss dominate the more metasomatized group. The mineral assemblage of highly metasomatized rocks include albite, K-feldspar, chlorite, epidote, titanite and magnetite; if present, the rare relics of primary minerals are heavily altered.

5.3.1. Amphibole

Amphibole in the least metasomatized amphibolite shows X_{Mg} [= Mg/(Mg + Fe²⁺)] = 0.53–0.57, Ti = 0.15–0.21 atoms per formula unit (apfu), Al = 1.87–2.18 apfu, (Na + K)_A = 0.43–0.5 and Cl/K = 0.16–0.27 (Fig. 9a, b; Table DRT1a). In comparison, amphibole from the more metasomatized amphibolite and amphibole gneiss have wider range of X_{Mg} (0.52–0.67), higher Cl/K (0.45–0.79; one at 1.03), and lower Ti (0.02–0.2 apfu), Al (0.71–2.02 apfu), and (Na + K)_A (0.06–0.57) (Fig. 9a, b; Table DRT1a). Amphibole (replacing clinopyroxene) from the least metasomatized gabbro is characterized by X_{Mg} = 0.36–0.43, Ti = 0.25–0.34 apfu, Al = 2.16–2.49 apfu, (Na + K)_A = 0.73–0.83 and Cl/K = 0.01–0.08 (Fig. 9a, b; Table DRT1b), while amphibole (replacing clinopyroxene) from the more metasomatized gabbro shows higher and wider range of X_{Mg} (0.43–0.55) and Cl/K (0.05–0.16), and lower Ti (0.05–0.24 apfu), Al (1.05–1.87 apfu), and (Na + K)_A (0.18–0.53) (Fig. 9a, b; Table DRT1b).

5.3.2. Clinopyroxene

 $\begin{array}{c|cccc} The & composition & of & clinopyroxene & varies & from\\ Wo_{49-51.7}En_{22.6-31}Fs_{18.9-26.5} \text{ in the least metasomatized gabbro to Wo_{47.}\\ 3_{-49.2}En_{28.6-34}Fs_{18.2-22.6} \text{ in the more metasomatized varieties (Fig. 9c;)} \end{array}$

Table DRT2). In addition to the difference in the Wo content, the clinopyroxene in the more metasomatized gabbro has lower X_{Mg} (0.56–0.65) and MnO content (0.28–0.63 wt%) than clinopyroxene in the least metasomatized gabbro ($X_{Mg} = 0.46-0.62$; MnO = 0.6–0.75 wt%) (Fig. 9c; Table DRT2). The Al₂O₃ content of clinopyroxene is comparable in the variants of gabbro [0.34–1.51 wt% (least metasomatized); 0.19–1.71 wt% (more metasomatized); Table DRT2].

5.3.3. Feldspar

The anorthite [An = Ca/Ca + Na + K)*100] content of plagioclase in amphibolite and amphibole gneiss varies in the range 53–71 mol% (Table DRT3a). It is 42–66 mol% in plagioclase from gabbro (Table DRT3b). Albite (1–8 mol% An) is present in the metasomatized amphibolite and amphibole gneiss (Table DRT3a). It is more common in leucocratic amphibolite than in the melanocratic one, and amphibole gneiss Albite (1–11 mol % An) is less common in the metasomatized gabbro (Table DRT3b). Orthoclase content of K-feldspar varies within 75–98 mol % in the leucocratic amphibolite and amphibole gneiss (Table DRT3a).

5.3.4. Chlorite

Chlorite is abundant in the metasomatized rocks. It is more common in leucocratic amphibolite than the melanocratic one, amphibole gneiss and gabbro (Figs. 5, 6, 8a, 9g–i, k, m–o and DR6 to 11). Different modes of occurrence of chlorite (replacing amphibole/clinopyroxene, intergrown with epidote, crisscrossing veins and bands) form two groups in terms of X_{Fe} [= Fe/(Fe + Mg)]: low X_{Fe} (0.35–0.43) and high X_{Fe} (0.58–0.73) (Table DRT4). Fe-rich chlorites occur in the more metasomatized rocks. Both groups of chlorite have comparable Al [4.46–4.99 apfu (low X_{Fe}); 4.59–5.25 apfu (high X_{Fe})], Mn [0.04–0.05 apfu (low X_{Fe}); 0.04–0.08 apfu (high X_{Fe})], and Ca [0.004–0.144 apfu (low X_{Fe}); 0.007–0.043 apfu (high X_{Fe})] contents (Table DRT4).

5.3.5. Epidote

Epidote is more common in leucocratic amphibolite than the melanocratic one, amphibole gneiss and gabbro. Similar to chlorite, the different modes of occurrence of epidote (replacing amphibole/clinopyroxene, riming earlier minerals, intergrown with chlorite, criss-crossing veins and bands; Figs. 5–7, 9g–k and DR6 to 11) form two groups in terms of Fe content – low-Fe (0.07–2.58 wt%) and high-Fe (7.7–15.29 wt%) (Fig. 9d; Table DRT5a,b). High-Fe epidote is prominent in more metasomatized amphibolite and amphibole gneiss, while low-Fe epidote occurs in partly–more metasomatized gabbro and partly metasomatized amphibolite–amphibole gneiss (Fig. 9d). Few epidote analyses from amphibolite and gabbro fall between the two groups (Fig. 9d). The low-Fe epidote have a restricted Al₂O₃ (21.97–24.11 wt%) and high-F CaO (24.91–26.98 wt%) content than the high-Fe epidote (Al₂O₃ = 20.21–26.6 wt%; CaO = 22.11–23.95 wt%; Table DRT5a,b).

5.3.6. Titanite

Similar to epidote, titanite is more common in leucocratic amphibolite than the melanocratic one, amphibole gneiss and gabbro. The titanite in metasomatized gabbro (Fig. 7b–f and DR11) are characterized by low Fe (0.01–0.03 apfu) and Al (0.04–0.06 apfu) (Fig. 9e; Table DRT6a). In comparison, the titanite in metasomatized amphibolite and amphibole gneiss (Fig. 6a, b, d, 9i, k and DR8) are characterized by high and wider ranges of Fe (0.02–0.05 apfu) and Al (0.05–0.23 apfu) than gabbro (Fig. 9e; Table DRT6b). The low Fe/Al ratio of titanite in gabbro, amphibolite and amphibole gneiss (<0.6; Table DRT6a,b) is comparable to that of titanite of hydrothermal origin (inset in Fig. 9e; Kowallis et al., 2022).

5.3.7. Apatite

The apatite in the partly metasomatized amphibolite, amphibole gneiss, and gabbro have lower F (1.33-2.91 wt%) and higher and wider Cl (0.07-1.44 wt%) content in comparison to those in the more



Fig. 8. Representative BSE images (a, b) and photomicrographs (c-h) illustrating the prominent effect of metasomatism on sulphides in gabbro, amphibolite and amphibole gneiss. (a), (b) Locally, the margins of sulphide grains are broken down and dispersed in gabbro. In comparison to gabbro, there is widespread effect of metasomatism in amphibolite and amphibole gneiss. Three patterns are observed in these rocks. (c), (d) Pattern 1 – sulphide grains were broken down into smaller fragments, and carried away by chlorite \pm epidote aggregates. (e), (f) Pattern 2 – sulphide grain margins are dusted to smaller grains and scattered by chlorite \pm epidote aggregates. (g), (h) Pattern 3 – sulphide grains are thinned down parallel to chlorite \pm epidote microveins and carried away. Po – pyrrhotite; Pn – Pentlandite; Cpy – chalcopyrite. (c)–(h) taken under reflected light. Inset in (g) taken under PPL. Additional images in DR12.



Fig. 9. Representative mineral chemistry based diagrams illustrating the compositional variation of individual minerals from less to the more metasomatized amphibolite, amphibole gneiss and gabbro. (a) X_{Mg} versus Cl/K of amphibole. (b) X_{Mg} versus Al_{tot} (apfu) of amphibole. (c) X_{Mg} versus Ca/(Ca + Mg + Fe²⁺) of clinopyroxene. (d) Al₂O₃ versus FeO (wt. %) of epidote. (e) Al (apfu) versus Fe (apfu) of titanite. Inset (axes same as the main diagram) is a compilation of titanite of hydrothermal origin from Kowallis et al. (2022). (f) F (wt. %) versus Cl (wt. %) of apatite. Insets are respectively lower right portions of triangular plots Mn-Na-Ca/100 and Mn-Fe-Ca/100, illustrating the comparison of apatite in the studied samples to those of altered apatite from low-T hydrothermal systems [fields from Dorais et al. (1997) and Piccoli and Candela (2002)]. (g)–(o) BSE images illustrating the effect of metasomatism in amphibolite and amphibole gneiss. (g) Epidote + chlorite intergrowth. (h) Epidote + chlorite veins crisscross the metasomatized rocks. (i), (j) Altered apatite (Ap) is commonly associated with titanite, epidote and chlorite. (k) Epidote, chlorite, titanite, albite and K-feldspar are conspicuous of more metasomatized rocks. (l) illuenite is often altered in metasomatized rocks. (m)–(o) Magnetite (Mt) is commonly associated with chlorite and are often broken down into smaller grains. Pyrite (Py) can be seen in (n).

metasomatized rocks (F = 3.82-6.18 wt%; Cl = 0.01-0.2 wt%) (Fig. 9f; Table DRT7). Apatite in the more metasomatized rocks is commonly associated with chlorite, epidote and titanite (Fig. 9i, j, m). In general, the Si-, Na- and Fe-rich composition (Table DRT7) is comparable to that of altered apatite (insets in Fig. 9f; Dorais et al., 1997; Piccoli and Candela, 2002). No monazite was found associated with apatite.

5.3.8. Ilmenite and magnetite

Ilmenite in the least metasomatized amphibolite and gabbro are characterized by higher Ti (7.93–8 apfu) and Mg (0.012–0.021 apfu), and lower Fe (7.44–7.91 apfu) than those in the more metasomatized rocks (Ti = 7.5–7.6 apfu; Mg = 0.003–0.006 apfu; Fe = 8.23–8.42 apfu) (Table DRT8); the latter can be altered (Fig. 91). Magnetite is associated with chlorite and epidote in the more metasomatized amphibolite (common in leucocratic amphibolite than the melanocratic one) and amphibole gneiss, and are often broken into smaller grains (Fig. 9m–o). In terms of composition, magnetite is characterized by a wide range of Ti (0.002–0.48 apfu) and Fe (22.41–23.91 apfu) (Table DRT8).

5.4. Whole-rock geochemistry

Variations of whole-rock composition between less metasomatized and more metasomatized rocks allow specification of the elemental lossgain pattern during metasomatism of amphibolite, amphibole gneiss and gabbro. Mass balance during metasomatism was evaluated for four sets of rock types: (1) (amphibole-rich) melanocratic amphibolite - less metasomatized rock GB10 versus more metasomatized rock GB11 from a c.1 m wide exposure from the Maope Hills, (2) (plagioclase-dominant) leucocratic amphibolite - less metasomatized rock MA1 versus more metasomatized rock GA1 from a c.1 m wide exposure from the Maope Hills, (3) amphibole gneiss - greyish-pink rock LCMQ7 versus pinkish rock LCMQ8 / pinkish rock LCMQ9 from a c.2 m wide exposure from the Maope quarry (degree of metasomatism increases from greyish-pink to pinkish rock; K-feldspathization is prominent in LCMQ8; albitization is prominent in LCMQ9); and (3) gabbro - less metasomatized rock GB13 versus more metasomatized rock GB14 from a c.1 m wide exposure from the Masikate Hills. In addition, two deep pinkish rocks (LCMQ10, LCMQ13) associated with the amphibole gneiss, and representing extreme stage of metasomatism (degree of metasomatism: LCMQ13 >LCMQ10), from the Maope quarry were also sampled. LCMQ10 is interbanded with amphibole gneiss, while LCMQ13 represents a massive domain associated with the gneiss. Garnet is absent in all the studied samples. The major, trace and REE data are listed in supplementary online material Table DRT9.

Following the Zr/Ti versus Nb/Y classification (Winchester and Floyd, 1977; Pearce, 1996) (inset in Fig. 10a; Table DRT9) the melanocratic amphibolite [SiO₂ = c.44–47 wt%; TiO₂ = c.0.4–1.9 wt%; Mg# $[100xMg/(Mg + Fe^{2+}); FeO = Fe_2O_3/1.15] = c.52-59]$, leucocratic amphibolite [SiO₂ = c.51 wt%; TiO₂ = c.0.3–0.4 wt%; Mg# = c.62–68] and gabbro [SiO₂ = c.49 wt%; TiO₂ = c.1 wt%; Mg# = c.53-54] are basaltic in composition, whereas the amphibole gneiss $[SiO_2 = c.52-56]$ wt%; TiO₂ = c.0.7–1.2 wt%; Mg# = c.50–52] is and esitic-dacitic in composition. Amphibole gneiss shows more fractionated REE pattern than amphibolite and gabbro (Fig. 10b; Table DRT9). The deep pinkish rocks associated with the amphibole gneiss [SiO₂ = c.58-68 wt%; TiO₂ = c.0.4–1 wt%; Mg# = c.54–57] show comparable fractionated REE pattern (Fig. 10b). The primitive mantle-normalized multi-element diagram clearly demonstrates the enrichment of the different rock types in LILE like Rb, Ba and K (Fig. 10a), that correlates with the observed extent of metasomatism inferred from petrography. The Cu, Ni and Co contents decrease from the less metasomatized rocks (65.2-29.2 ppm; 219-49 ppm; 91.7-24.7 ppm, respectively) to the more metasomatized ones (54.2- 6.8 ppm; 135-24 ppm; 71.4-10 ppm, respectively) (Table DRT9). Simple mass balance analysis (Gresens, 1967; Grant, 1986) between the less and more metasomatized varieties of the four rock types indicates that Na₂O, K₂O and SiO₂ were gained, while FeO

and MgO were lost during metasomatism (Fig. 10c-f; Table DRT9). The progress of albitization and/or K-feldspathization results in the gain of Na₂O or K₂O and loss of MgO, FeO, MnO, TiO₂ [Fig. 10g, h; MgO + FeO + MnO + TiO₂ = c.12 wt% (LCMQ7) to c.4 wt% (LCMQ13)]; Table DRT9). The gain/loss pattern of the deep pinkish rock LCMQ13 represents the extreme stage of metasomatism (Fig. 10h).

5.5. Geochronology

5.5.1. ⁴⁰Ar/³⁹Ar amphibole geochronology

⁴⁰Ar/³⁹Ar geochronology on fabric-forming minerals (e.g., amphibole, mica) is a method commonly used to date overprint events like metasomatism (McDougall and Harrison, 1999; Kelley, 2002; Reiners et al., 2005). Amphibole from two metasomatized amphibolite (GB15, GB17), and amphibole replacing clinopyroxene respectively from a least metasomatized (MA2) and a more metasomatized (MA4) gabbro (Fig. 2c for locations) were subjected to ⁴⁰Ar/³⁹Ar analysis. Amphibole is locally replaced by epidote along its margins in the least metasomatized gabbro MA2 (e.g., Fig. 7a). Amphibole in the metasomatized amphibolite GB15 and GB17, and gabbro MA4 are variably replaced by chlorite \pm epidote. There is no evidence for anatectic overprint in the dated amphibolite and gabbro. The Ar analytical data, including Ca/K and Cl/K ratios, which are useful to get a better approximation of overprint ages (e.g., Villa et al., 2000), are listed in supplementary online material Table DRT10. In the 40 Ar/ 39 Ar spectra, a plateau age is characterized by at least five or more consecutive apparent age segments that are equal within the 2σ error, and that account for more than 50 % of total ³⁹Ar released (Schaen et al., 2021). In this study, the terms pseudo-plateau and plateau are respectively used to highlight relatively fewer consecutive steps in the age spectrum. ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ step heating of amphibole grains from the two metasomatized amphibolite respectively yielded plateau [78 % of 39Ar (GB15)] and pseudo-plateau [74 % of 39Ar (GB17)] with integrated ages of 2013 \pm 14 Ma (GB15; Fig. 11a) and 2006 \pm 14 Ma (GB17; Fig. 11b). The corresponding Ca/K and Cl/K ratios are 40.66 and 0.54 (GB15), and 24.47 and 0.43 (GB17) (Table DRT10). ⁴⁰Ar/³⁹Ar step heating of an amphibole grain from the least metasomatized gabbro MA2 yielded a plateau (94 % of ³⁹Ar) with an integrated age of 2013 \pm 12 Ma (Fig. 11c), while that from the metasomatized gabbro MA4 yielded a pseudo-plateau (79 % of ³⁹Ar) with an integrated age of 1882 \pm 19 Ma (Fig. 11d). The corresponding Ca/K and Cl/K ratios are 10.17 and 0.04 (MA2), and 16.5 and 0.11 (MA4) (Table DRT10). In all the cases, minor low-temperature heating steps include older ages (Table DRT10). Also, there is good correspondence of Cl/K and Ca/K ratios from amphibole mineral chemical data and ⁴⁰Ar/³⁹Ar geochronology (Fig. 11e, f; Tables DRT1a, b and 10).

5.5.2. U-Pb titanite geochronology

Because of its ability to grow in magmatic, metamorphic and metasomatic environments, titanite is increasingly used for U-Pb geochronology (Corfu, 1996; Frost et al., 2001; Kohn, 2017). Titanite in a metasomatized gabbro slightly away from the eastern branch of the Dikalate Shear Zone (Fig. 2c for location) was subjected to U-Pb geochronology. Analyses were performed in situ in thin section of the metasomatized gabbro (LC5) using LA-MC-ICPMS. The isotopic composition of titanite from LC5 are listed in supplementary online material Table DRT11, and plotted in the Tera-Wasserburg concordia diagram (Fig. 11h). Errors in corrected ratios are reported as 1σ , and uncertainties in intercept ages are reported as 95 % confidence limits. Representative BSE image of titanite with analytical spots and numbers, corresponding to the data in Tables DRT11, are given in Fig. 11g.

Thirty-three LA-ICPMS analyses were carried out on titanite grains from sample LC5. The common Pb in these grains are negligible. Thirty-two least discordant (<16 %) analyses of titanites gave apparent 206 Pb/ 238 Pb ages between 1974 Ma and 2057 Ma. They correspond to U contents of 14–26 ppm, Th contents of 62–131 ppm and Th/U ratios of 3.3–5.0 (Tables DRT11). One analysis with lower U (3 ppm) and Th (13



Fig. 10. Primitive mantle normalized trace element spider (a) and chondrite normalized REE (b) diagrams (Sun and McDonough, 1989) of less and more metasomatized variants of melanocratic amphibolite, leucocratic amphibolite, gabbro, amphibole gneiss and deep pinkish rock associated with amphibole gneiss. Inset in (a) shows the same rock compositions in a Zr/Ti (TiO₂*0.0001) versus Nb/Y volcanic classification diagram of Winchester and Floyd (1977) and Pearce (1996). (c)– (h) Diagrams highlighting whole-rock major element gain/loss pattern ($\Delta C_i/C_i^0$) related to metasomatized rock assuming for the less-more metasomatized rock pairs used in the study. $\Delta C_i/C_i^0$ represents change for elements between the less and more metasomatized rock assuming no volume change. Abbreviations in terms of cation elements used in the diagrams. The respective rock types and degree of metasomatism in each case is indicated in the diagrams.



Fig. 11. 40 Ar/ 39 Ar spectra of amphibole in metasomatized amphibolite GB15 (a) and GB17 (b), and that of amphibole replacing clinopyroxene in least metasomatized gabbro MA2 (c) and more metasomatized gabbro MA4 (d). Uncertainty limits are indicated in 95% confidence. Ca/K versus Cl/K diagrams comparing the amphibole mineral chemical characteristics obtained from electron microprobe and 40 Ar/ 39 Ar analyses for amphibolite (e) and gabbro (f). (g) Representative BSE image of titanites in metasomatized gabbro LC5 with analytical spots and numbers, corresponding to the data in Table DRT11. (h) Tera-Wasserburg diagram of all U-Pb titanite data from the metasomatized gabbro LC5. Ellipses indicate 1 σ uncertainty.

ppm) contents, and Th/U of 4.3 is more discordant (c.31 %). In a Tera-Wasserburg diagram, the bulk of the data points cluster together close to the concordia while the discordant point spread out, all lying on or close to a single chord that gives a lower intercept age of 1964 ± 14 Ma [mean squared weighted deviation (MSWD) = 6.6], and a meaningless upper intercept of c.4.3 Ga (Fig. 11h).

6. Discussion

6.1. Sequence of overprint events in the Masikate-Maope areas

Field relations and geochronologic data indicate three events which variably overprinted the rocks in the Masikate-Maope areas.

- Alkali metasomatism (2013 \pm 12 Ma; 2013 \pm 14 Ma; 2006 \pm 11 Ma; 1964 \pm 14 Ma; 1882 \pm 19 Ma; this study)
- Shear deformation (2013 \pm 8 Ma; Rajesh et al., 2020a)
- Anatectic overprint (2056 ± 12 Ma; 2020 ± 5 Ma; Zeh et al., 2009; Basupi et al., 2022)

6.2. Amphibole replacing clinopyroxene in gabbro

The formation of brownish amphibole after clinopyroxene in gabbro (Fig. 7a, e) is earlier than the pervasive metasomatism forming epidote, chlorite, titanite, albite and sericite, and need to be addressed separately. Similar textures (e.g., brownish amphibole rimming pyroxene) have been reported from a gabbronorite in the southern Maope Hill (Basupi et al., 2022; Rajesh et al., 2023). Significantly, the chemical characteristics of amphibole replacing pyroxene in the gabbro and gabbronorite are comparable. Phase equilibria modelling showed pressure about 5 kbars and temperature 770-780 °C for the formation of amphibole after pyroxene in gabbronorite, while ⁴⁰Ar/³⁹Ar geochronologic data attested an age of 2037 \pm 27 Ma for the process (Rajesh et al., 2023). Thus, as inferred for the gabbronorite (Basupi et al., 2022; Rajesh et al., 2023), the formation of brownish amphibole after clinopyroxene in gabbro (Fig. 7a, e) is likely related to the infiltration of aqueous fluids during the retrograde stage of evolution in the Masikate-Maope areas.

6.3. Sequence of metasomatic assemblages in the rocks

Amphibole and clinopyroxene in the different rocks are replaced by chlorite and epidote. The progress of metasomatism results in a pervasive formation of these minerals (Figs. 5 to 7, 9 and DR6 to 11). In view of the replacement of amphibole along grain margins by chlorite or epidote in the least metasomatized rocks, chlorite seems to form before epidote in the melanocratic amphibolite, while it is later than epidote in the leucocratic amphibolite, amphibole gneiss and gabbro (Figs. 5 to 7 and DR6 to 11). Titanite forms during metasomatic reactions (Figs. 6, 7 and DR8, 11), whereas magnetite becomes characteristic for the more metasomatized rocks (Fig. 9). Sericite, albite and K-feldspar progressively replace plagioclase, with K-feldspar restricted to leucocratic amphibolite and amphibole gneiss (Figs. 5 to 7, 9 and DR6 to 11). The metasomatic replacement is most prominent in the plagioclasedominant rocks in comparison to the amphibole and/or clinopyroxene-rich ones. The number of phases decreases from the least metasomatized to more metasomatized rocks (Figs. 5 to 7 and DR6 to 11) in accordance with the Korzhinskii theory of metasomatism (Korzhinskii, 1968). In addition, there are clear progressive compositional changes of rocks from the least metasomatized to more metasomatized rocks (Fig. 9). The enrichment of Na, K, Si and depletion of Fe, Mg (Fig. 10) can be accounted by the dissolution of mafic phases accompanied by albitization and K-feldspathization during alkali metasomatism. The prominent role of aqueous fluids in causing dissolutionprecipitation in feldspars is well understood (Putnis et al., 2007; Engvik et al., 2008; Hövelmann et al., 2010). Involvement of an aqueous fluid is substantiated by the formation of hydrous minerals in the studied rocks. The extent of sericitization indicates that the studied plagioclasebearing rocks have undergone extensive recrystallization and subsolidus re-equilibration (Plümper and Putnis, 2009). Local reddish variant of the extensively metasomatized rock is likely due to the presence of iron oxides (Nakano et al., 2005; Putnis et al., 2007: Norberg et al., 2014).

6.4. Phase equilibria modelling

To evaluate the progress of the metasomatic reactions and sequences of mineral assemblages in different rock types, $lg(a_{K2O})$ - $lg(a_{H2O})$ diagrams (pseudosections) have been constructed for representative rock compositions of melanocratic amphibolite (GB10), leucocratic amphibolite (GA1), amphibole gneiss (LCMQ7) and gabbro (GB14) (Tables DRT9 for compositions; Figa. 12a–d). Details of pseudosection modelling are given in supplementary online material DR2. Pseudosections were computed in the system Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–O₂

(NCKFMASHTO) using the PERPLE_X software (Connolly, 2005) for temperature 440 °C as average temperature responsible for formation of the Ep + Chl + Ab assemblage in the studied rocks (based on P-T pseudosection for the amphibolite GB10). In addition, albitization of plagioclase, which is common in all the studied metasomatized rocks, typically occurs at temperatures below 450 °C (Nijland and Touret, 2001). Pressure 5 kbar was taken for the calculation based on our previous study of high-temperature hydration of gabbronorite from the Maope Hill (Rajesh et al., 2023).

The diagrams for four samples show comparable topology (Fig. 12a–d). The fields involving K-feldspar (pale pink fields) and the fields involving chlorite never overlap being separated by the region involving mica (sericite). The widest K-feldspar-bearing regions are observed for the leucocratic amphibolite GA1 (Fig. 12a) and the amphibole gneiss LCMQ7 (Fig. 12b), whereas it is strongly reduced (displaced toward higher a_{K20} values) for the melanocratic amphibolite GB10 (Fig. 12c). This represents the formation of K-feldspar via predominant replacement of plagioclase. The higher the plagioclase content in the starting rock, the more active formation of K-feldspar in it. This fact reliably explains why leucocratic amphibolite and amphibole gneiss are visually more affected by pinkish discoloration manifesting K-feldspar development in comparison to melanocratic varieties.

An influx of a K-bearing fluid with the arbitrary a_{H2O} and a_{K2O} marked by a yellow star on the pseudosections results in formation of new assemblage of Ep + Kfs + Ab in both leucocratic rock types (Fig. 12a, b). Epidote (without K-feldspar) could be formed also via increase of a_{H2O} at constant low a_{K2O} (Fig. 12a–d). Nevertheless, it is clearly seen from the pseudosection of GA1 (Fig. 12a) that epidote can appear at lower water activity via the increase of a_{K2O} . This phenomenon can be explained by an operation of the model reaction (abbreviations after Whitney and Evans, 2010).

$2An (in Pl) + 2Qz + [1/2K_2O + 1/2H_2O] (in fluid) = Czo (in Ep) + Kfs(1)$

Decomposition of anorthite component of plagioclase results in the formation of albite, which is common mineral in the metasomatized rocks. The reaction (1) is low-temperature analogy for the reaction forming grossular-rich garnet and K-feldspar after plagioclase via increasing alkali activity recorded in plagioclase-rich rocks interacting with salt-bearing fluids under granulite and amphibolite facies conditions (e.g., Safonov and Aranovich, 2014; Aranovich and Safonov, 2018).

An arbitrary evolution of the fluid shown by a white dashed arrow in the pseudosections (increase of a_{H2O} and decrease of a_{K2O}) results in formation of mica (sericite) and, eventually, chlorite (Fig. 12a, b). The final assemblage Ep + Chl + Ms + Ab + Ttn + Qz in the leucocratic rocks forms at the highest $a_{\rm H2O}$, which is probably related to a decrease of alkali activity. The same variations of a_{K2O} and a_{H2O} would produce no K-feldspar in the melanocratic amphibolite, although albite forms because of extraction of Ca from plagioclase to form epidote (Fig. 12c). The same trend of the $a_{\rm K2O}$ and $a_{\rm H2O}$ variation would visually resemble the hydration process in the melanocratic rock. In contrast to leucocratic rocks, chlorite forms before epidote in the melanocratic amphibolite, whereas the final assemblage is $Amph + Ep + Chl + Ttn + Ab \pm Qz$ (Fig. 12c). This sequence fully agrees with petrographic observations on the melanocratic amphibolite GB10. The effect of fluid variation in this case is recorded just in a slight decrease of the Ti, Al, Na + K contents of amphibole because of the formation of epidote, chlorite, albite and titanite.

K-feldspar is not observed (or very minor) in the gabbro manifesting no visible effect of metasomatism. The $a_{\rm H2O}$ - $a_{\rm K2O}$ space of K-feldspar-

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Fig. 12. The $lg(a_{K2O})-lg(a_{H2O})$ pseudosections constructed at 440 °C and 5 kbar for representative rock compositions of leucocratic amphibolite GA1 (a), amphibole gneiss LCMQ7 (b), melanocratic amphibolite GB10 (c), and gabbro GB14 (d). Transparent pale pink field combines phase fields involving K-feldspar. Pink line marks the Kfs-in phase boundaries, magenta line marks the Ep-in phase boundaries, green line marks the Chl-in phase boundaries. Yellow star shows an arbitrary parameters of a fluid interacting with the rocks, and white dashed line is an arbitrary trend of the fluid evolution (see text).

bearing assemblages in the pseudosection for the gabbro GB14 is comparable to that for the leucocratic amphibolite and the amphibole gneiss (Fig. 12d). Nevertheless, there is still a relatively narrow a_{H2O} - a_{K2O} region, which is within the K-feldspar bearing assemblages for the leucocratic amphibolite and the amphibole gneiss, but is beyond the Kfeldspar bearing assemblages for gabbro (compare Fig. 12d and 12a, b). Thus, a possible increase of a_{K2O} would show no visible effect in the gabbro (i.e., K-feldspatization) or it would be negligible. Further hydration produces Ep + Ab + Ttn and, subsequently, chlorite, so the final assemblage in the gabbro is Ep + Chl + Ab + Ttn \pm Qz replacing clinopyroxene and amphibole (Fig. 12d), consistent with petrographic observations.

6.5. Extent of metasomatism in southeastern Motloutse Complex

Different stages of metasomatism are widely distributed along an E-W section between the Masikate-Maope areas (Fig. 2c, d). Metasomatized rocks are conspicuously located within and proximal to the Dikalate Shear Zone and its branches (the mapped extent of the shear zones are shown as dashed lines in Fig. 2d). However, not all sheared rocks are metasomatized. For example, although a progressive increase of strain is seen in sheared ultramafic rocks (supplementary online material Fig. DR13) exposed along the eastern branch of the Dikalate Shear Zone, they do not exhibit any visible effect of alkali metasomatic overprint. Another exception to the rule is the dioritic amphibole gneiss exposed at the Maope quarry, towards the western extremity of the study area (Fig. 2c). Although these rocks are not associated with any shear structures, they are heavily metasomatized (Fig. 4). In tonalite gneiss and amphibolite, the pinkish discoloration marks earlier structures such as layering, folds, boudins, shear planes etc. (Fig. 3 and DR4). Contacts between rock types is another important site for infiltration of metasomatic fluids (e.g., between tonalite gneiss and amphibolite; Fig. 3a). However, contacts between the melanocratic and leucocratic amphibolite, as well as with gabbroic rocks are not visibly affected by metasomatism. Active fluid infiltration at a local scale is highlighted by the massive epidote-rich zones following pre-existing fabric (Fig. DR5c). Thus, in spite of the active role of earlier structures, including shear zones, it is important to take into account the difference in rock composition, the fluid/rock ratio and the relative duration and intensity of fluid influx as additional factors defining the spatial distribution of metasomatism. Example of the ultramafic rock versus dioritic amphibole gneiss demonstrate that the presence or absence of feldspar likely played a major role in recording the effect of alkali metasomatism. In terms of the fluid/rock ratio, although the voluminous felsic rocks (tonalite gneisses) experienced extensive fluid infiltration, the less voluminous mafic rocks (amphibolites) facilitated massive concentration of mineralized (epidote) zones related to metasomatism. Last, but not least, in view of the progressive nature of metasomatism, the impact of the relative duration and intensity of fluid influx is important to understand, as more intensive influx of fluids likely occurred during the later stages of metasomatic overprint. In the case of rapid fluid influx, structures related to fluid overpressure (e.g., Boudreau, 1992; Boorman et al., 2003) could be formed at a local scale, and need to be kept in mind in future studies in the Masikate-Maope areas.

6.6. Timing of metasomatism in southeastern Motloutse Complex

Garnet porphyroblasts associated with anatexis in amphibolite are broken down into smaller grains, and carried away by chlorite + epidote + sericite aggregates (Fig. DR10), indicating that the metasomatism is younger than c.2.02 Ga. The conspicuous following of the pinkish discoloration of shear planes (Figs. DR4d-f, h) argue for a time frame of c.2.01 Ga or younger for the metasomatism. The composition of amphibole progressively replaced by epidote and chlorite in the more metasomatized amphibolite (Fig. 5 and DR6, 7) is different from that of amphibole in least metasomatized amphibolite (Fig. 9a, b). Thus the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 2013 \pm 14 Ma and 2006 \pm 14 Ma obtained from these amphiboles are argued to date metasomatism. The pseudo-plateau (Fig. 11b) is likely due to the relatively high altered nature of amphibole in the respective metasomatized amphibolite (Fig. 11e). In the case of least metasomatized gabbro, epidote locally replace brownish amphibole along its margins (e.g., Fig. 7a). Hence, the $^{40}\mbox{Ar}/^{39}\mbox{Ar}$ age of 2013 ± 12 Ma obtained from amphibole replacing clinopyroxene likely dates the beginning of metasomatic overprint in gabbro. The plateau nature of the age (Fig. 11c) correlates with the less metasomatized nature of the dated gabbro (Fig. 11f). In comparison, the pseudo-plateau 40 Ar/ 39 Ar age of 1882 \pm 19 Ma correlates with the highly metasomatized nature of the dated gabbro (Fig. 11f), thereby defining a younger limit to the metasomatic event. The U-Pb age of 1964 \pm 14 Ma for titanite, which forms at the expense of clinopyroxene, amphibole and ilmenite in metasomatized gabbro, melanocratic-leucocratic amphibolite and amphibole gneiss (Figs. 6, 7, 9 and DR8, 11) brackets the metasomatic event in southeastern Motloutse Complex to c.2.01-1.96 Ga.

6.7. Implications for sulphide mineralization (and exploration)

Both the Selebi-Phikwe (within the Phikwe Complex) and the Masikate-Maope (within the Motloutse Complex) areas have comparable geological structure including ultramafic (peridotite-pyroxenite) and mafic (amphibolite, gabbro, anorthosite) rocks occurring as dismembered remnants within granitoid gneiss. Like in the Selebi-Phikwe deposits, sulphides are primarily hosted in amphibolite from the southeastern Motloutse Complex. The prominence of sulphide in melanocratic amphibolite than the leucocratic one from the Masikate-Maope areas (this study) is comparable to the scenario at Selebi-Phikwe, where massive sulphide layers occur in amphibole-rich mafic amphibolite with the content of disseminated sulphide decreasing towards the plagioclase-dominant feldspathic amphibolite (Fig. DR1; Brown, 1988). Other noticeable sulphide occurrence in the Selebi-Phikwe area are in gabbronorite, peridotite and pyroxenite (Gordon, 1973; Wakefield, 1976; Marsh, 1978; Brown, 1988; Maier et al., 2008). Although no sulphides occur within the ultramafics (Rajesh et al., 2022b), they are prominent in gabbro from the Masikate-Maope areas. But there are important differences between the Selebi-Phikwe and the Masikate-Maope scenarios. There is evidence for a prominent granulite-facies metamorphic overprint in mafic rocks of the Phikwe Complex (Hickman and Wakefield, 1975; Lear, 1971; Key et al., 1976; Aldiss, 1983; Holzer et al., 1999; Zeh et al., 2009). Effects of high-grade tectonometamorphic and polyphase deformation are preserved in the Selebi-Phikwe host rocks and ore textures (Gordon, 1973; Wakefield, 1976; Marsh, 1978; Brown, 1988). No such pervasive granulite-facies metamorphic overprint is seen in the southeastern Motloutse Complex. Significantly, there is no report on the alkali metasomatic overprint from the Selebi-Phikwe Ni-Cu sulphide deposits. Notwithstanding the role of hydrothermal fluids in remobilizing, transporting and reprecipitating the sulphide-bearing elements in amphibolite at Selebi-Phikwe, in the case of the Masikate-Maope rocks, the sulphides were broken down and dispersed by the prominent alkali metasomatic overprint (Fig. 8 and DR12). A probable reason for this difference in overprint events is because unlike the scenario for southeastern Motloutse Complex, the sulphide deposits within the Phikwe Complex are not spatially related to a terrane boundary. This brings into picture the role of the Dikalate Shear Zone and its branches (Fig. 2c, d) in promoting alkali metasomatism in southeastern Motloutse Complex.

6.8. Possible source and setting for metasomatic fluids

The medium-grade Motloutse Complex and adjacent high-grade terranes of Phikwe Complex and Beit Bridge Complex (Fig. 13) represents different Paleoproterozoic crustal levels (Holzer et al., 1998; Van Reenen et al., 2008; Brandt et al., 2023). High-pressure (P > 10 kbar) rocks characterize the lower crustal Beit Bridge Complex, whereas the Motloutse Complex is composed of medium-pressure (P = 7 kbar) upper-middle crustal rocks (Brandt et al., 2023; Rajesh et al., 2023). There is evidence for the presence of lower crustal alkaline fluids underneath the Beit Bridge Complex in Paleoproterozoic. For example, the Madiapala syenite massif (M in Fig. 13) is considered as the result of 2010 \pm 5 Ma (U-Pb titanite; Rigby and Armstrong, 2011) syenitization of the regional (Alldays) TTG gneiss by alkali fluids (Seliutina et al., 2020). In such a scenario, the fluids that caused metasomatism at c.2.01–1.96 Ga in southeastern Motloutse Complex are likely of upper crustal origin.

If the metasomatic overprint affected both the Limpopo and Motloutse complexes (Fig. 13; next section), then the source of fluids has to be from a larger geologic entity that is proximal to both terranes. This suggests the role of fluids exsolved from the c.2.06–2.04 Ga Bushveld large igneous province (Bushveld LIP), which covers a large area in southern Africa including adjacent regions of the Limpopo Complex (dashed line in inset of Fig. 13; Rajesh et al., 2013a; Ernst, 2014). There is evidence for the voluminous action of aqueous and saline fluids released from magmas to contact aureoles of the Bushveld LIP (Mathez



Fig. 13. Generalized outline map of the medium-high-grade metamorphic terranes and sub-terranes of the Limpopo and Motloutse complexes between the Zimbabwe and Kaapvaal cratons in southern Africa summarizing the available ages on Paleoproterozoic shear deformation (in purple color) and metasomatic overprint (in blue color). c.2.04–2.03 Ga ages on metasomatic overprint from the Southern Marginal Zone and Beit Bridge Complex are separately indicated (in green color). The approximate extent of the large alkali metasomatic province (LAMP) defined in the study is shown as grey filled region. Nsz – Nthabalala Shear Zone. Inset in (b) is a satellite image of southern Africa showing the known extents of Zimbabwe and Kaapvaal cratons. The dashed line and the highlighted (yellow) units indicate the known extent of the Bushveld large igneous province (LIP) (Rajesh et al., 2013a; Ernst, 2014). The orange rectangle indicate the approximate extent of the area covered in the main map.

et al., 1994; Willmore et al., 2000; Gleason et al., 2011; Benson et al., 2021; Zhou et al., 2021). However, there is a notable time gap between the waning phase of the Bushveld LIP (c.2.04 Ga) and the beginning of the metasomatic overprint deduced for the Motloutse Complex (c.2.01 Ga). This can be reconciled by taking into consideration the metasomatic and shear deformation events that happened during the period c.2.04-2.01 Ga. Different studies argued for a c.2.04-2.03 Ga metasomatic overprint involving aqueous and saline fluids from wide localities in the Southern Marginal Zone and Beit Bridge Complex (Fig. 13; Buick et al., 2007; Safonov et al., 2012; Belyanin et al., 2014; Rajesh et al., 2013b, 2014; Zeh and Gerdes, 2014). These include granulites from the Southern Marginal Zone (G in Fig. 13; 2043 \pm 8 Ma; $^{40}\text{Ar}/^{39}\text{Ar}$ biotite: Belvanin et al., 2014), amphibolites and schists from the Venetia Klippe (V in Fig. 13; 2040 \pm 3 Ma; Lu-Hf zircon-garnet-whole rock isochron; Zeh and Gerdes, 2014), orthopyroxene-bearing dehydration zones from the Causeway locality, SE of Musina (C in Fig. 13; 2037 ± 10 Ma; ⁴⁰Ar/³⁹Ar amphibole; Rajesh et al., 2014) and alteration zones in amphibolites from near the Tshipise Shear Zone (T in Fig. 13; 2030 \pm 2 Ma; U-Pb titanite; Buick et al., 2007). This was followed by a prominent c.2.01-1.95 Ga (details in next section) transpressive event involving strike-slip shearing along the shear zones that crisscross the Limpopo-Motloutse complexes and separate them from adjacent cratonic domains (Fig. 13; Barton et al., 1994; Kamber et al., 1995a; Jaeckel et al., 1997; Holzer et al., 1998, 1999). Combining the above information, we propose a model where the fluids exsolved from the Bushveld LIP penetrated the adjacent medium-high-grade terranes. The Paleoproterozoic reactivation of the regional shear zones that crisscross the terranes facilitated the pervasive infiltration of these fluids, with the consequent effects of metasomatism covering a wide area (next section).

6.9. Arguments for a large alkali metasomatic province (LAMP) in southern Africa

A summary of available ages on Paleoproterozoic shear deformation and metasomatic overprint from the Limpopo and Motloutse complexes is given in Fig. 13. There is a prominent alkali metasomatic event in the southeastern Motloutse Complex (2013 \pm 12 Ma to 1964 \pm 14 Ma; this study) related to the Dikalate Shear Zone (2013 \pm 8 Ma; Rajesh et al., 2020a), which separates the Motloutse and Phikwe complexes (Fig. 13). Similar extensive alkali metasomatism proximal to the Magogaphate Shear Zone near its contact with the Dikalate Shear Zone is primarily manifested in the pinkish to reddish discoloration of the large porphyritic alkali granite body at the Dikalate Hills [large magnetic body around Dikalate up to the east of Masikate in Fig. 2a, b (reddish to pinkish in 2a)]. Available geochronologic constraints from the Magogaphate Shear Zone include c.2 Ga Rb-Sr biotite, 2001 \pm 6 Ma PbSL titanite and 1997 \pm 7 Ma Pb-Pb apatite ages (Fig. 13; Van Breemen and Dodson, 1972; Holzer et al., 1999). Alkali metasomatism accompanying shear deformation and related to the Sunnyside Shear Zone is a prominent overprint in the southern part of the Motloutse Complex, near the contact with the northern Mahalapye Complex (Fig. 13). The shear deformation and metasomatism along the southern Motloutse Complex are respectively dated at 1987 \pm 7 Ma and 1951 \pm 11 Ma (Fig. 13; 40 Ar/ 39 Ar biotite; Rajesh et al., 2022a).

Alkali metasomatic overprint is reported from the southeastern part of the Phikwe Complex near its contact with the Beit Bridge Complex, and available geochronologic data indicate an age of c.1.93 Ga (Fig. 13; unpublished U-Pb zircon overgrowth age; Thatayaone, 2021). Although the nature of the contact is not clear, shear deformation and associated pinkish discoloration of rocks is reported from the contact zone of the Phikwe and Beit Bridge complexes (Thatayaone, 2021). Alkali metasomatic overprint is widely distributed in the Beit Bridge Complex, which is the largest unit of the Central Zone of the Limpopo Complex. The 2010 \pm 5 Ma age (U-Pb titanite; Rigby and Armstrong, 2011) from the Madiapala syenite massif dates the alkali metasomatism event (Fig. 13). Ages of 2020 \pm 8 Ma to 1971 \pm 26 Ma are reported for shear deformation within the > 20 km wide Tshipise Shear Zone/Palala Shear Zone, that separates the Central Zone from the Southern Marginal Zone (Fig. 13: McCourt and Vearncombe, 1992: Holzer et al., 1998, 1999: Schaller et al., 1999; Belluso et al., 2000). Metasomatic alteration within and near the Tshipise Shear Zone is dated between 2015 \pm 7 Ma and 2007 ± 5 Ma [Pb-Pb/Pb-Pb step wise leaching (PbSL) titanite; Holzer et al., 1998; Buick et al., 2003]. Pinkish discoloration of rocks occurs proximal to the Palala Shear Zone and Mahalapye Shear Zone (Fig. 13; Key, 1979; Rabewu, 2016; Ntema, 2016). This metasomatic overprint has to be younger than c.2.02 Ga, i.e., the age of sheared alkali granites in the region (McCourt and Armstrong, 1988).

Metasomatic alteration marked by pinkish discoloration of host rocks along shear zones (Hout River Shear Zone, Nthabalala Shear Zone, Petronella Shear Zone) is prominent in the Southern Marginal Zone of the Limpopo Complex (Fig. 13; Du Toit, 1994; Smit and Van Reenen, 1997; Tsunogae and Van Reenen, 2014; Van Reenen et al., 2014). Both Neoarchean and Paleoproterozoic ages are available for the metasomatic overprint in Southern Marginal Zone. In contrast to the Neoarchean fluid activity of CO₂-rich fluids (e.g., Huizenga et al., 2014; Safonov et al., 2014, 2018), the Paleoproterozoic alkali metasomatic overprint was related to shear deformation [2027 ± 11 Ma to 2013 ± 8 Ma (40 Ar/ 39 Ar amphibole, mica; Belyanin et al., 2014); 1976 ± 11 Ma to 1925 ± 19 Ma (U-Pb zircon overgrowth; Rajesh et al., 2020b); c.1.9 Ga (Rb-Sr mica; Barton and Van Reenen, 1992)], but its extent within the Southern Marginal Zone need to be clarified.

In contrast to the Southern Marginal Zone, alkali metasomatic overprint is not known from the Northern Marginal Zone of the Limpopo Complex. Nevertheless, there is evidence for shear deformation in the Paleoproterozoic. Ages of 1971 \pm 11 Ma to 1951 \pm 17 Ma reported from local shear zones in the northeastern part of the Northern Marginal Zone are related to retrograde fluid evolution (Fig. 13; PbSL titanite; 40 Ar/ 39 Ar biotite; Kamber et al., 1996). Shear deformation along the c.30–50 km wide Triangle Shear Zone that separates the Northern Marginal Zone and the Central Zone, is dated between 2040 \pm 15 Ma to 1984 \pm 12 Ma, with a prominent set of ages from 2001 \pm 11 Ma to 1955 \pm 8 Ma (Fig. 13; 40 Ar/ 39 Ar amphibole; Kamber et al., 1995a, 1995b). In the suggested model of the Paleoproterozoic alkali metasomatism related to the Bushveld LIP, the difference in the extent of metasomatic overprint between the two marginal zones of the Limpopo Complex can be explained by their different proximity to the LIP (Fig. 13).

In summary, the alkali metasomatism reported in this study from the southeastern Motloutse Complex is not an isolated event, but part of a regional event, which covers the adjacent medium–high-grade terranes of the Limpopo and Motloutse complexes (Fig. 13). Based on the extent of this phenomenon and available ages, we argue for a c.2.01–1.95 Ga large alkali metasomatic province (LAMP) in southern Africa (Fig. 13). The broadly contemporaneous timing of the shear deformation along the different terrane boundaries and metasomatic overprint argues for the shear zones as leading pathways for fluid migration (e.g., Newton, 1990; Fossen and Cavalcante, 2017). Nevertheless, additional age data are necessary from other areas to further delineate the southern African LAMP (Fig. 13).

7. Concluding remarks

- Alkali metasomatic overprint marked by varying degrees of pinkish discoloration and associated yellowish green to greenish epidote veins/bands/aggregates is prominent in rocks exposed within and closer to the Dikalate Shear Zone and its branches in Masikate-Maope areas, southeastern Motloutse Complex.
- The metasomatic reactions in amphibolites, gabbro and amphibole gneiss involved replacement of amphibole, clinopyroxene, ilmenite and plagioclase with chlorite, epidote, titanite, magnetite, sericite, albite and K-feldspar. With increasing degrees of metasomatism, earlier minerals get broken down and dispersed.
- Mineral chemical characteristics highlight a progressive compositional evolution from the less to more metasomatized rocks. Whole rock geochemical trends of enrichment of Na, K, Si and depletion of Fe, Mg between the less and more metasomatized rocks indicate the dissolution of mafic phases accompanied by albitization and Kfeldspathization during alkali metasomatism.
- The modeling of mineral assemblages in terms of the lg(a_{K2O})–lg (a_{H2O}) pseudosections indicates that the metasomatic process involved an increase of potassium activity followed by hydration. Chloritization, epidotization, sericitization and albitization proceeded in amphibole \pm clinopyroxene-bearing rocks, while K-feld-spathization became active later on in plagioclase-dominant rocks.
- According to the proposed model, alkaline fluids migrating along shear zones progressively metasomatized the rocks. The model is supported by geochronologic data on shear deformation (c.2.01 Ga) and metasomatic overprint (c.2.01–1.96 Ga) from the Masikate-Maope areas.
- The results highlight the cause-and-effect antithetic relation between metasomatism and ore sulphide mineralization: the metasomatic overprint resulting in the break down and dispersal of the Cu-Ni sulphide minerals in the amphibolite, gabbro and amphibole gneiss.
- It is suggested that the alkali metasomatic event recognized in southeastern Motloutse Complex is not isolated, but part of a wider c.2.01–1.95 Ga Large Alkali Metasomatic Province (LAMP) in southern Africa covering the medium–high-grade terranes of Limpopo and Motloutse complexes between the Zimbabwe and Kaapvaal cratons.
- The fluids are likely sourced from post-emplacement exsolution of the c.2.06–2.04 Ga Bushveld LIP, while the c.2.01–1.95 Ga reactivation of shear zones that crisscross the medium–high-grade terranes facilitated the pervasive migration of fluids, leaving behind footprint over a wide area.

CRediT authorship contribution statement

H.M. Rajesh: Conceptualization, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. O.G. Safonov: Investigation, Methodology, Writing – review & editing. G.A. Belyanin: Investigation, Methodology, Visualization. K.P. Letshele: Investigation, Validation, Visualization. C. Vorster: Investigation, Methodology, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.precamres.2024.107402.

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