Phase relations of aenigmatite minerals in a syenitic ejectum, Wonchi volcano, Ethiopia

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Abstract

Wonchi volcano (Ethiopia) is the second locality for wilkinsonite, the new mineral related to aenigmatite via the coupled substitution $2Fe^{3+} = TiFe^{2+}$. Wilkinsonite occurs as relics surrounded by rims of riebeckite and biotite in a syenitic ejectum which also contains microphenocrysts of aenigmatite. The two minerals do not represent an equilibrium pair. They both formed in the magma chamber under plutonic to hypabyssal conditions, but during two following stages of crystallisation separated by a major drop in f_{O_2} conditions.

KEYWORDS: aenigmatite, wilkinsonite, syenitic ejectum, Wonchi volcano, Ethiopia.

Introduction

Two aenigmatite-group minerals, one Ti-bearing (aenigmatite) and another Ti-free (wilkinsonite), occur within a syenitic ejectum in the inner caldera of Wonchi volcano, Ethiopia. They do not represent an equilibrium pair: wilkinsonite is a relic, armoured against the groundmass by an inner riebeckite and an outer biotite rim, whereas aenigmatite is a microphenocryst in equilibrium with the same groundmass of the ejectum. We discuss the possible significance of this non-equilibrium assemblage in relation to the evolution of igneous activity of Wonchi, an explosive central volcano located on the northern side of the Ethiopian Rift.

Materials

Wonchi volcano is located some 20 km south of Hagere Hiywot (Ambo), a town of Showa 90 km west of Addis Ababa (Ethiopia) on the road to Nekempt. This majestic volcano (3456 m high and 50 km in diameter) overlooks the Guraghe plain which consists mainly of upper Pliocene stratoid pyroclastic deposits of trachytic to rhyolitic composition attributed to the Balchi formation (Zanettin and Justin-Visintin, 1974). Wonchi volcano is located south of the major tectonic alignment known as the Addis Ababa-Nekempt line (Abbate and Sagri, 1980), and is therefore believed to be related to the same acidic volcanic activity that formed numerous volcanic cones to the north-west of the East African Rift in the surroundings of Addis Ababa (e.g. Yerer, Wachacha, Zuquala, etc.), all dated ca. 4.5 Ma (Zanettin et al., 1980).

The volcanic edifice, formed mostly of fine-grained, poorly consolidated pyroclastic high-energy deposits, is very complex, with numerous calderas and satellite craters. In particular, the innermost and probably most recent caldera, now filled by a lake, has walls consisting of very fine-grained ash-grey pyroclastics carrying scattered rounded whitish ejecta of variable grain-size and appearance (Gaeta and Mottana, in preparation).

One of these ejecta, unusually coarse-grained and massive but also showing small vugs among the interlocking feldspar phenocrysts, was sampled at an elevation 2980 m on the path from the market place alongside the newly built Ambo-Waliso road down to the lake and to Wonchi village. The ejectum shows silica-saturated syenitic composition and a holocrystalline granular texture tending to ophitic. It consists of large albite ($Ab_{96}Or_4$) phenocrysts (70 vol%) embedded in a finer-grained groundmass (20 vol%) made up of albite + microcline ($Ab_{22}Or_{78}$, usually showing patchy exsolutions of finely twinned albite), and with microphenocrysts of deep red aenigmatite + brown amphibole + emerald green clinopyroxene (all together ca. 10 vol%).
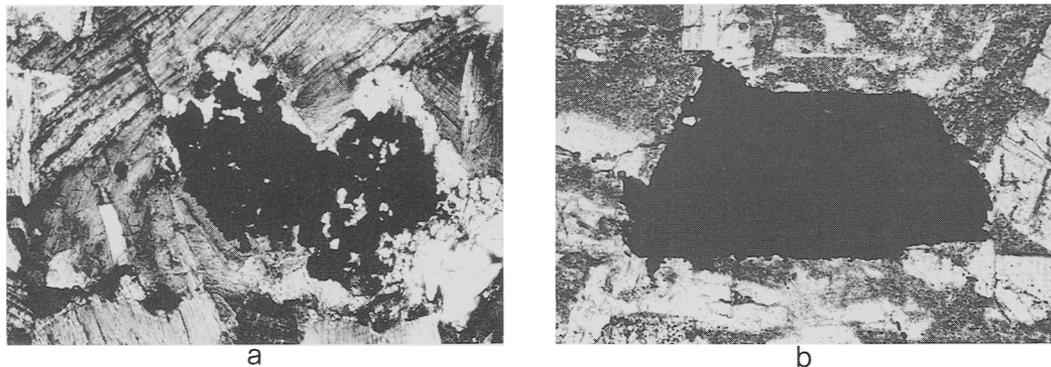
Aenigmatite is homogeneous. Amphibole is

FIG. 1. (*a*) Textural relationships in a clot: innermost core (dark) is wilkinsonite; the first rim is riebeckite (bluish); and outer rim is biotite (brown). (*b*) Euhdral microphenocrysts of aenigmatite (dark) in the groundmass. Horizontal field of view is 1 mm for both pictures.

zoned outwards from sodian-(titanian-potassian-manganoan) edenite to calcian (titanian-potassian-manganoan) arfvedsonite to (potassian-titanian-manganoan) arfvedsonite (nomenclature after Leake, 1978). Clinopyroxene is also zoned outwards from aegirine-augite to titanian aegirine (nomenclature after Morimoto *et al.*, 1988).

Scattered in the groundmass are small, dark lobate clots (1 × 3 mm in size) consisting of a concentric association of a completely opaque mineral (core), bluish amphibole (first rind), and large brown biotite flakes (rim). Fig. 1 shows the textural relationships.

Methods

Microprobe analyses were carried out on the same polished thin sections used for petrographic examination, using a Link AN 10000 85/S energy-dispersive system fitted on a Jeol JXA 50A instrument running at 15 kV and 2 nA, and standardised on Co metal. The standards used were mostly natural: albite from Amelia, sanidine and jadeite from Burma, olivines from Norway and from Eagle Station; but also synthetic diopside glass and metals (Ti, Cr). Raw data were reduced by the built-in program of the Link apparatus, which is based on the ZAF procedure. Partition of Fe into Fe^{2+} and Fe^{3+} was made by the stoichiometric method (Droop, 1987). Analyses and formulae are given in Table 1.

Results

The coloured minerals occurring in the ejectum are mostly very complex solid solutions, where elements which are usually minor, like Ti, K, and Mn, can play a significant role. Feldspars, on the contrary, are binary solid-solutions lying on the Or–Ab compositional join, the An component always being nil.

Aenigmatite, present as euhedral phenocrysts (Fig. 1*b*) of millimetric size, is close to the theoretical end-member composition $Na_2Fe_5^{2+}TiSi_6O_{20}$, since it only shows partial substitution of Mn for Fe^{2+}. As most aenigmatites in lavas (cf. Deer *et al.*, 1978) it contains no K or Ca. In the Ti–(Mg + Mn + Fe^{2+})–Fe^{3+} diagram (modified after Cosca *et al.*, 1988, Fig. 2) it plots near the apex of the divalent cations. All microphenocrysts are inclusion-free, sharply contoured, and isolated within the groundmass. Only one is found associated with a manganous ilmenite, and rimmed by a very thin, needle-like layer of Ti-rich ferrous biotite (annite).

The opaque core of the clot (Fig. 1*a*), the most interesting mineral of the ejectum, is characterised with respect to aenigmatite not only by the absence of Ti, but also by a drastic drop of SiO_2, coupled by an equally drastic increase of FeO_{tot}. The high Fe_{tot} determined by the microprobe can be partitioned by stoichiometry (assuming 14 cations over a total of 20 oxygens) into a major Fe_2O_3 portion and a minor FeO one. Despite the considerable uncertainty inherent in this procedure (which Larsen, 1977, estimates to be 0–30% relative for reliable analyses and 50–100% for those affected by serious errors), such a high Fe_2O_3 content identifies this aenigmatite mineral as wilkinsonite (Duggan, 1990), the newly discovered Ti-free member of the group from the lavas of Warrumbungle volcano, Australia, also subsilicic volcano (Duggan, 1988).

Wilkinsonite is characterised by the complete substitution of 1 Ti with 1 Fe^{3+} in the octahedral sites, balanced by the oxidation of an equal

amount of Fe^{2+} to Fe^{3+}. In our wilkinsonite, Fe^{3+} is present not only in the octahedral, but also in the tetrahedral sites. These are deficient because their low Si is not compensated by the trifling Al + Cr present, and need to be brought up to 6 by considering *ca.* 30 mol% of a hypothetical 'Fe^{3+}-tschermakitic component', analogous to that proposed by Larsen (1977) to explain the complex solid-solution-system of certain aenigmatites of the Ilímaussaq intrusion, Greenland.

Our wilkinsonite presents some other additional oddities.

(*a*) The Na1–Na2 sites (nomenclature after Cannillo *et al.*, 1971) contain significant Ca and K in addition to Na. The former cation is not unusual in aenigmatites, and actually emphasises with its presence the structural relationship existing between aenigmatite and rhönite (Bonaccorsi *et al.*, 1990), nor is it unusual in our sample when compared with those listed e.g. by Deer *et al.*, 1978. As for the latter cation, our sample is apparently the most potassian member of the aenigmatite group ever found.

(*b*) The octahedral sites contain minor but significant amounts of Mg and Mn. While other aenigmatites are known that contain Mn in higher amounts than ours (e.g. 0.527 at p.f.u.; Marsh, 1975), there is no other containing as much Mg (cf. Deer *et al.*, 1978).

(*c*) The high octahedral Fe^{3+} sets our sample, in the triangular plot (Fig. 2*b*), between type-wilkinsonite and dorrite, another mineral belonging to the aenigmatite group but with Ca > Na (Cosca *et al.*, 1988). As a confirmation of the local very high Fe^{3+} content, the only inclusions we found in our wilkinsonite are tiny grains of manganian hematite.

In the Wonchi ejectum wilkinsonite appears to be a typical relic (Fig. 1*a*). It is anhedral in shape, and consists of several fragments of an originally continuous large crystal. The various fragments are joined together by a layer of coarse biotite flakes that is the product of the reaction with the groundmass. However, wilkinsonite was preserved from complete alteration to biotite because it is armoured by a thin layer of amphibole (Fig. 1).
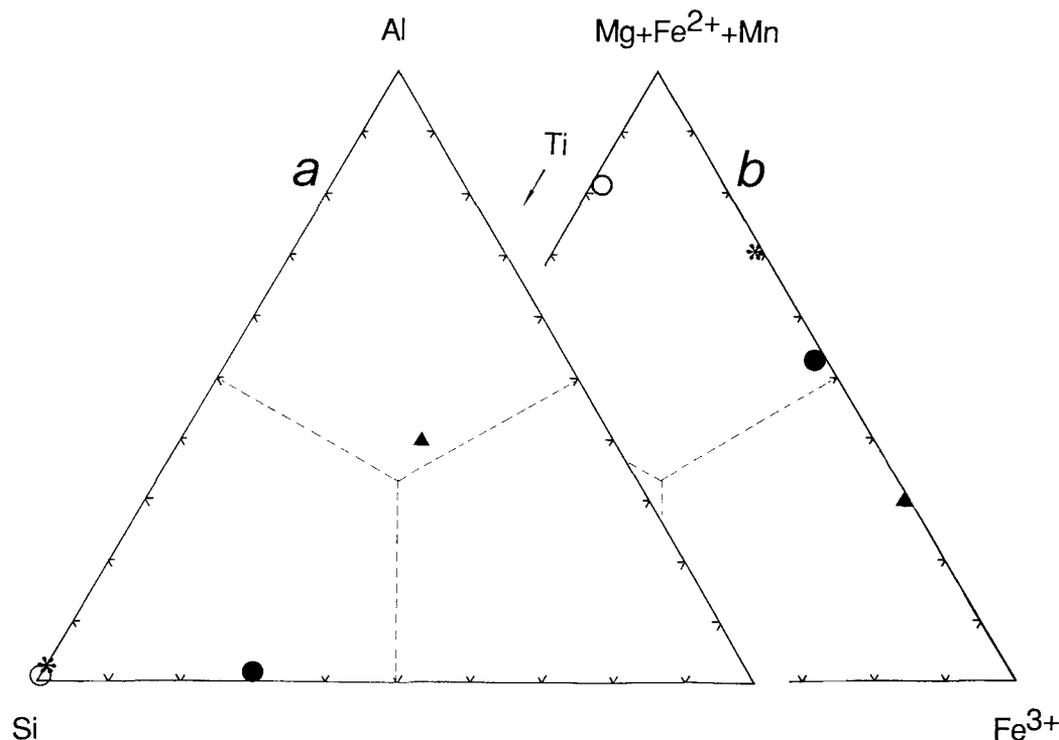

FIG. 2. Projection of wilkinsonite (dot) and aenigmatite (circle) in terms of tetrahedral occupancy (Si–Fe^{3+}–Al triangle) and octahedral occupancy (Ti–(Mg + Fe^{2+} + Mn)–Fe^{3+} triangle). Modified after Cosca *et al.*, 1988. As reference, wilkinsonite from the type-locality (Duggan, 1990) is also shown (star) and dorrite (Cosca *et al.*, 1988) as a triangle.

TABLE 1: Representative electronmicroprobe analyses of the clots assemblages and of the aenigmatite in the groundmass.

Mineral Points	Wlk 5		Rbk 7	Bt 8	Agm 7
SiO_2	29.29	(1.57)	50.15	33.21	40.43
TiO_2	0.04	(0.02)	0.03	0.00	9.44
Al_2O_3	0.06	(0.02)	0.61	8.58	0.46
Cr_2O_3	0.06	(0.06)	0.02	0.00	0.00
Fe_2O_3	41.53	(2.69)	3.84	4.47	0.00
FeO	14.34	(1.70)	21.95	32.14	37.34
NiO	0.15	(0.09)	0.00	0.00	0.20
MnO	2.07	(0.20)	2.26	3.37	3.70
MgO	5.50	(0.49)	6.69	3.51	0.05
CaO	0.68	(0.02)	1.47	0.02	0.00
Na_2O	5.94	(0.34)	8.87	0.62	7.46
K_2O	0.75	(0.02)	1.28	8.16	0.00
Tot.	100.41		97.17	94.11	99.08
Si	4.274		7.672	5.690	5.829
Ti	0.004		0.003	0.000	1.023
Al	0.010		0.109	1.733	0.078
Cr	0.007		0.003	0.000	0.000
Fe^{3+}	4.560		0.441	0.577	0.000
Fe^{2+}	1.749		2.809	4.606	4.501
Ni	0.018		0.000	0.000	0.023
Mn	0.256		0.293	0.489	0.451
Mg	1.196		1.525	0.896	0.011
Ca	0.106		0.241	0.003	0.000
Na	1.680		2.631	0.206	2.084
K	0.140		0.274	1.783	0.000
Tot.	14.000		16.001	15.983	14.000

Value in brackets is the standard deviation. Wlk=wilkinsonite; Rbk=riebeckite; Bt=biotite; Agm=aenigmatite. Formulae computed on the basis of 14 metal ions for WKL and Agm, 13 (-Ca, -K, -Na) for Rbk, and 14 (-Ca, -K, -Na) for Bt, after Droop (1987).

This amphibole differs from the amphiboles of the groundmass (which are mostly of arfvedsonitic composition: see above) by being a *riebeckite* (Table 1), and is completely homogeneous in composition. Again, its chemistry presents some oddities; Mg and Mn are significant, although not extreme, and K, in particular, in unusually high. In marked contrast with the armoured wilkinsonite, riebeckite has a very low $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ value of 0.14.

The surrounding *biotite* has an even lower $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio (0.11), and furthermore concentrates Mn, a divalent cation, with respect to both riebeckite and wilkinsonite. The high Al and K contents of the biotite obviously derive from the reacting feldspar phase. The feldspar in contact is a phenocrystic homogeneous albite ($Ab_{96}Or_4$), but the feldspar phase more likely to be involved in the reaction is the groundmass K-feldspar, now of composition $Ab_{22}Or_{78}$ and

triclinic in symmetry, but originally considerably more sodic (it displays numerous albite exsolutions) so as to fall in the anorthoclase compositional field, as we found in other ejecta which did not undergo the exsolution process (Gaeta and Mottana, in preparation).

Discussion

Aenigmatite is a scarce but not rare mineral occurring in many peralkaline to transitional lavas produced by advanced differentiation from basalts in oceanic islands and in continental rift zones (e.g. Barberi et al., 1982; Baker, 1982). It occurs also in alkali-syenitic plutonic rocks, produced from differentiation of gabbros (e.g. Hodges and Barker, 1973; Grapes et al., 1979; Larsen, 1977). Wilkinsonite, on the other hand, has only recently been found in a mildly silica-unsaturated peralkaline trachyte (Duggan, 1988, 1990).

The occurrence of wilkinsonite at Wonchi volcano, within a syenitic ejectum crystallised at plutonic to hypabyssal depths, enlarges the pressure range for the stability field of this phase, but poses questions on the relative stability of the various phases the aenigmatite–rhönite group. The occurrence in the same specimen of two phases which are isostructural but differ greatly in composition may imply the existence of equilibrium relationships such as a miscibility gap, as it has been postulated between aenigmatite and rhönite (Yagi, 1953; Grunhagen and Seck, 1972; Grapes et al., 1979). However, at Wonchi textural relationships definitively rule out the possibility that aenigmatite and wilkinsonite are in equilibrium.

Wilkinsonite grew around, and at the expense of hematite in an oxidised silica-deficient environment rich in Mg, Mn, Ca and K which became incorporated to unusually high extents within the growing phase. Aenigmatite grew instead in a nearly silica-saturated environment, at hematite-free sites and in association with ilmenite, when f_{O_2} had been reduced to the point that little or no Fe^{3+} was present in the magma that could be incorporated into the forming phases, and when the activities of Ti and Mn had become very high.

According to most researchers (e.g. Carmichael, 1962; Yagi and Souther, 1974; Grapes et al., 1979; Duggan, 1988) aenigmatite would not precipitate from a peralkalic liquid unless during the late stage, when the Ti activity becomes high enough despite the limited bulk amount of Ti in the magma. On the other hand, Larsen (1977) found at Ilímaussaq that the Mg and Ca contents of aenigmatites decrease as crystallisation pro-

ceeds, whereas Mn increases with crystallisation. If such a trend has a general significance, the Mg- and Ca-rich wilkinsonite of Wonchi is an early differentiation product that crystallised without removing Ti, so that the latter could increase in the magma until aenigmatite became stable. Aenigmatite, on the other hand, is the last product of the entire differentiation process that concentrated all of the Ti remaining in the final liquid.

However, this simple relationship does not emphasise adequately a major environmental feature, the strong change in the oxygen fugacity regime undergone by the crystallising magma.

Crystallisation of Fe^{3+}-rich wilkinsonite after hematite indicates high f_{O_2} conditions, far above those of the iron–wüstite (IW) and wüstite– magnetite (WM) buffers at which the pure wilkinsonite end-member was first synthesised (Ernst, 1962). Duggan (1990) suggests that reduced silica activity is the factor stabilising wilkinsonite in the Warrumbungle lavas, at f_{O_2} conditions that may be as high as the fayalite– magnetite–quartz (FMQ) buffer. This does not seem to be the case at Wonchi, since the ejectum is silica-saturated. As an alternative stabilising factor we indicate pressure, which is testified not only by the plutonic appearance of the ejectum, but also by the high amount of Mg incorporated in wilkinsonite (cf. the relative stability of mag- nesiostaurolite and staurolite, or of magnesiocar- pholite and carpholite). On the other hand, the high temperature of formation of wilkinsonite can be deduced from incorporation in the structure of large cations such as K and Ca.

Therefore, we are inclined to believe that f_{O_2} had to be even higher than that for FMQ during formation of wilkinsonite, of the order of the hematite–magnetite (HM) buffer, also under consideration of the Mn content of hematite present (bixbyite component).

After formation of hematite and wilkinsonite a major drop in f_{O_2} intervened in the Wonchi magma chamber, destabilising wilkinsonite and changing the crystallisation conditions of the entire system. Riebeckite formed at the expense of wilkinsonite by a reaction involving strong reduction, but at the same time it kept in its structure minor elements diadochic to Fe^{2+} such as Mn and Mg. Moreover, more large cations, such as K and Ca (and the smaller Al), were taken from the magma. In particular, Ca was entirely removed from the magma, so that the feldspars that precipitated during the major crysallisation phase are Ca-free.

The reaction involving anorthoclase and rie- beckite to produce biotite is likely to be very late

in the cooling hystory of the Wonchi magma, since the formed biotite is not only strongly enriched in Mn, but it is totally Ti-free, as against the biotite fringes bordering aenigmatite. The relationships between these two types of biotite is puzzling: there is probably no relationship at all. However they grew independently, with their compositions controlled by their substrate, as illustrated by the fact that the former still contains a portion of Fe^{3+} and the latter only Fe^{2+} and no Mg.

Conclusions

Wilkinsonite crystallises in lavas cooled at ambient pressure as at the type locality, Warrum- bungle volcano (Duggan, 1990), but also under the moderate pressure characteristics of a magma chamber still in the plutonic environment. In such a case it is enriched in Mg and large cations such as Ca and K with respect to wilkinsonite in lavas.

The early precipitation of wilkinsonite from the cooling magma does not disturb the trend of Ti- enrichment by which weakly saturated to under- saturated peralkaline magmas acquire the chemi- cal composition appropriate to precipitate aenig- matite from their residual liquids. However, such a trend is also accompanied by, and perhaps involves, a drastic reduction of f_{O_2} probably as a result of the removal of Fe^{3+}-bearing phases (wilkinsonite, aegirine-augite, arfvedsonite), so that these liquids will finally crystallise with separation of aenigmatite in a reduced environment.

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