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Extreme chemical conditions of crystallisation of Umbrian Melilitolites and wealth of rare, late stage/hydrothermal minerals

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Abstract: Melilitolites of the Umbria Latium Ultra-alkaline District display a complete crystallisation sequence of peculiar, late-stage mineral phases and hydrothermal/cement minerals, analogous to fractionated mineral associations from the Kola Peninsula. This paper summarises 20 years of research which has resulted in the identification of a large number of mineral species, some very rare or completely new and some not yet classified. The progressive increasing alkalinity of the residual liquid allowed the formation of Zr-Ti phases and further delhayelite-macdonaldite mineral crystallisation in the groundmass. The presence of leucite and kalsilite in the igneous assemblage is unusual and gives a kamafugitic nature to the rocks. Passage to non-igneous temperatures (T$<$600 °C) is marked by the metastable reaction and formation of a rare and complex zeolite association (T$<$300 °C). Circulation of low-temperature (T$<$100 °C) K-Ca-Ba-CO_2-SO_2-fluids led to the precipitation of sulphates and hydrated and/or hydroxylated silicate-sulphate-carbonates. As a whole, this mineral assemblage can be considered typical of ultra-alkaline carbonatitic rocks.

Keywords: melilitolite • ultra-peralkaline liquid • Zr-Ti minerals • zeolites • hydroxylated silicate-sulphate-carbonates • Umbria Latium Ultra-alkaline District

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1. Introduction

Two similar associations of late stage and hydrothermal minerals in melilitolites from the Umbria Latium Ultra-alkaline District [1] show a number of extreme chemical features, as well as a wealth of peculiar mineral species which are rare and only observed in deposits associated with peralkaline and carbonatitic igneous rocks. Distinctive accessory/rare minerals comprise Zr-Ti disili-cates, rhodesite group minerals and K–Ca zeolites. Low-temperature, contact/metasomatic minerals include Calcium Silicate Hydrate (CSH) and Calcium Aluminium Silicate Hydrate (CASH) cement minerals [2]. These associations' geological context, relationship with encasing host rocks and liquid composition require a comparative study in order to understand their origin, possible economic utility and for their disclosure to a wider scientific audience. However, the lure of the perfect and stunning crystalline forms and the rarity of some of these minerals indicate the need for more than mere structural and compositional data collection, as well as the importance of understanding the value of the mineralogical association itself to stimulate

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further study. The large number of mineral species present (up to 100, some not yet identified) has thus far prevented the publication of a complete mineral list and accompanying photographic record. The present paper summarises 20 years of mineralogical and petrological research in this area which has resulted not only in numerous publications but also the establishment of a volcanic park and museum in San Venanzo. The paper reviews detailed earlier reports together with new petrographic and mineral images of melilitolite minerals made available by various authors. Neogene to Quaternary magmatism in Italy has been attributed to subduction involving conventional trench retreat and back–arc extension [3]. However, the general picture is made more complicated by the peculiar chemical and isotopic variation of the associated magmatism [4, 5], with leucitites, kamafugites, carbonatites, lamprophyres and lamproites in particular challenging any subduction-related model [6]. High Field Strength Elements (HFSE) distribution is crucial; a review of Zr–Ti minerals found in these rocks may parallel the argument regarding the magmatogenetic context and would also help to form an understanding of the importance of the topic presented in this paper, as well as stimulate further reading.

2. Petrological context

Two leucite kalsilite melilitolite subvolcanic bodies occur at Colle Fabbri (Perugia Province, Umbria, Italy) and San Venanzo (Terni Province, Umbria, Italy), respectively, and belong to the Intra–mountain Ultra–alkaline Province (IUP) of Central Italy (Fig. 1a,b). This igneous district is characterised by kamafugite and carbonatite monogenetic volcanoes comprising diatremes, maars, tuff–rings, plug, dykes and lava flows [6, 7]. Subvolcanic bodies in particular display a well–developed contact facies showing a complete crystallisation sequence of late stage mineral phases and hydrothermal/cement mineral facies (Table 1). Umbria melilitolite essential minerals are typically found in many similar outcrops worldwide. Rock melilite modal abundance is >>10% and >65%, and leucite plus kalsilite >>10%, with the specific root name being kalsilite leucite melilitolite. Colle Fabbri rock on the other hand is correctly classified as kalsilite leucite wollastonite melilitolite [8]. The essential mineral assemblage corresponds to the crystal–liquid equilibrium expected in the leucite–wollastonite–melilite plane of the kalsilite –wollastonite–diopside – åkermanite system, i.e. Yoder's sub–tetrahedron [9], in which all the Umbrian melilitolites can be projected. Crystallisation in the leucite–åkermanite–SiO2 system is also essentially controlled by the Lc-(Di+Wo) and Sa-(Di+Wo) joins [10], leading to an assemblage
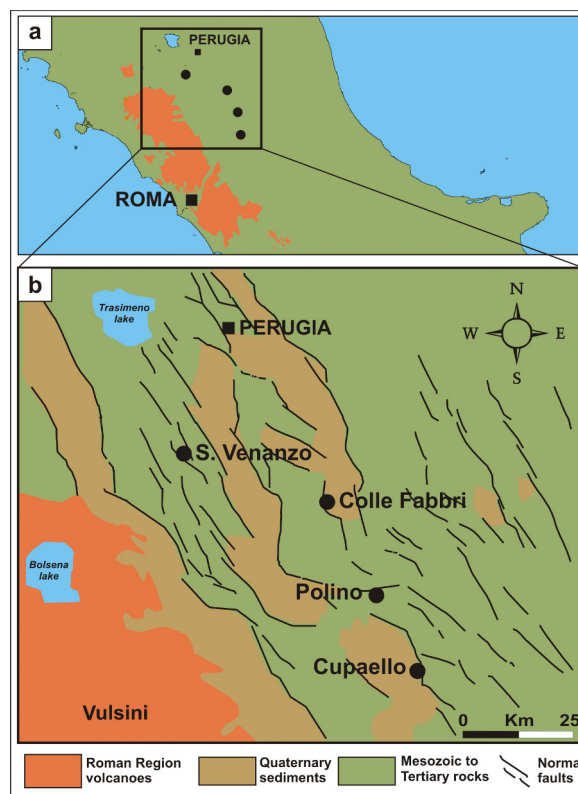
Figure 1. a- Geological sketch map of the volcanoes of the Roman Region; b- location of the San Venanzo and Colle Fabbri melilitolites, as well as other kamafugite and carbonatite centres of the Ultra-alkaline Umbrian District [1].

of wollastonite–melilite–leucite at T=1280 °C under atmospheric pressure, closely approaching that determined by fluid inclusion studies examining Umbrian melilitolites [11–13]. However, the progressive increasing alkalinity of the residual liquid allowed the formation of Zr–Ti phases and further delhayelite-macdonaldite mineral crystallisation in the groundmass.

2.1. Pian di Celle melilitolite

2.1.1. Field and petrological context

Coarse–grained, ocellar, kamafugitic melilitolite represents the final event in the development of the Pian di Celle volcano, one of the three emission centres of the San Venanzo volcanic complex [14]. It forms a main sill from which depart numerous dykelets intruding the Le Selvarelle kamafugitic lava [5, 11–16]. The rock contains tabular melilite up to 5 cm in length (Fig. 2a–b; Fig. 3b), olivine (Fig. 4a), leucite (Fig. 4c), fluorophlogopite and Ti–rich magnetite as essential minerals that resemble the fine–grained groundmass of the hosting lava. In-

terstices between essential phases are filled with a fine-grained groundmass consisting of Ti-rich magnetite, fluorapatite, fluorophlogopite, nepheline, kalsilite, clinopyroxene, Zr-Ti-disilicates (cuspidine, hiortdahlite, khibinskite), umbrianite, westerveldite, sulphides (pyrrhotite, bartonite, galena), ferroan monticellite to magnesian kirschsteinite, perovskite, fluorite and ilmenite (Fig. 2a-g; Fig 4e). A Cr-rich mineral of the magnesioferrite-magnetite series occurs as inclusions in the olivine. The majority of the groundmass phases occur as well-shaped crystals in voids which also contain vanadinite, rhodesite, chabazite-(Ca), phillipsite-(Ca), willhendersonite, thomsonite-(Ca) and apophyllite. Some insufficiently studied phases of melilitolite include Ca-Fe-H_2O- and Mg-H_2O-silicates, a macdonaldite-like mineral, a hydrodelhayelite-like mineral and a CuFe sulphide [16]. Abundant large ocelli of calcite (up to vol.20% of the rock) and green or brown silicate glass are an important constituent of the rock [11, 12, 16–18]. Crystallisation order: chromian spinel, perovskite ≈ olivine, nepheline, melilite ≈ apatite, magnetite, leucite, phlogopite, clinopyroxene ≈ kalsilite, götzenite, REE-rich perovskite, cuspidine, calcite ≈ khibinskite, sulphides, umbrianite, delhayelite, macdonaldite ≈ Ca-Fe-hydrosilicate ≈zeolites.

Late stage and contact facies

Most minerals of the late magmatic or hydrothermal stage are located in cavities that are framed by large crystals of melilite and leucite. It is believed that the angular shape and intergranular cavities were filled with carbonate (K-Na carbonates?) and other soluble salts now dissolved. In fact, the smallest intergranular volumes and some inclusions still contain these compounds [13]. However, it is not possible to know if this "soluble" component was dissolved by watering or by hydrothermal fluids. The latter hypothesis is reasonable and would explain not only some of the pseudomorphosis phenomena described later in the text but also the deposition of zeolites and other minerals at low temperatures. The carbonate ocelli are different, being clearly associated with liquid minerals of magmatic temperature and also shown to have plastically deformed the ground mass assemblage. Low temperature minerals do not occur in the ocelli that are regarded as the primary magmatic feature. A sophisticated micronalitic study would be able to determine how much of the carbonate associated with the magmatic minerals is primary and how much is secondary [19]. The zeolites and other lower temperature assemblages are known to be one of the richest and more peculiar described by various authors; further details can be found in Tables 1 and 2, and

Table 1. Synoptic table of groundmass, hydrothermal and epigenic "cement" minerals from San Venanzo and Colle Fabbri melilitolites, with a side-by-side comparison of minerals from the two localities and their main literature sources.

Mineral	Occurrence San Venanzo	Colle Fabbri	References
Tobermorite		X	[2]
Jennite		X	[2]
Afwillite		X	[2]
Ettringite		X	[2]
Thaumasite		X	[2]
Strätlingite		X	[20]
Vertumnite		X	[2]
Chabazite-Ca	X	X	[2, 29]
Levyne-Ca		X	[2]
Willhendersonite	X	X	[2, 29]
Gismondine		X	[2]
Phillipsite-Ca	X	X	[2, 29]
Ca-K zeolite (Merlinoite?)		X	[2]
Apophyllite-(KF)	X	X	[2, 15]
Apophyllite-(KOH)	X	X	[2, 15]
Aragonite		X	[2]
Calcite	X	X	[2, 29]
Gypsum		X	[2]
Barite		X	[2]
Pyrrhotite	X	X	[16]
Magnetite (Ti-rich)		X	[2]
Opaline silica		X	[2]
Tridymite		X	[2]
Portlandite		X	[2]
Umbrianite	X		[29]
Arfvedsonite	X		[29]
Zr-aegirine	X		[29]
Bartonite	X		[16]
Cuspidine	X		[11]
Hiortdahline	X		[12]
Götzenite	X	X	[15, 24]
Khibinskite	X	X	[12, 15]
Westerveldite	X		[16, 29]
Kirschsteinite	X		[29]
Monticellite	X		[29]
Thomsonite-Ca	X		[29]
Vanadinite	X		[29]
Chlorbartonite	X		[29]
Galena	X		[29]
Bafertisite group	X		[29]
Rankinite		X	[22]
Cordierite		X	[22]
Fe-Ni sulphides		X	[22]
Ti-rich Ca-alumosilicate		X	[22]
Indialite		X	[20]
Tridymite		X	[20]
Hydrated Ca-silicates		X	[20]
Hydrated complex sulphates		X	[20]

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Table 1. Contd.

Mineral	Occurrence		References
	San Venanzo	Colle Fabbri	
Ti-garnet		X	[13]
Ti-clinopyroxene		X	[13]
Magnetite		X	[13]
Perovskite		X	[13]
Apatite		X	[13]
Delhayelite	X		[16]
Macdonaldite	X		[16]
Hydrodelhayelite	X		[16]
Günterblassite	X		[29]
Hillesheimite	X		[29]

in Section 3.3. No particular variation has been observed at the contact, where melilitolite is fine-grained and where there are only scarce cavities.

2.2. Colle Fabbri melilitolite

2.2.1. Field and petrological context

Colle Fabbri is a stock which intrudes a 4 metre thick, phreatic breccia, whereas the conduit is excavated in Pliocene clay. The stock is 60 m wide, with outcrops of approximately. 500 m^2. Contact with wall rock exhibits strong thermal metamorphism [20]. The rock is classified as kalsilite leucite wollastonite melilitolite according to Dunworth and Bell [8] and the IUGS [21]. Forming euhedra up to 5 mm in length which enclose wollastonite and rankinite prisms, melilite shows anomalous blue-grey interference colours and a yellow rim (Fig. 3a,b), occasionally intergrowing with leucite and/or kalsilite. Leucite forms subeuhedral crystals with distinctive polysynthetic sector twinning (Fig. 3a,b; Fig 4b). Anorthite forms glomerules or small patches. Spinel forms zoned irregular grains or inclusions in other minerals. The characteristics of the textures suggest rapid crystallisation of the minerals from a liquid, with equally rapid co-precipitation of anorthite, wollastonite and melilite followed by lower temperature phases and eventually intergranular mesostasis. The intergranular component is composed of small grains of kalsilite, leucite, Zr-cuspidine, perovskite, Ti-garnet, zoned spinel, rankinite, Ti-Al-Fe^{P3+}-clinopyroxene, apatite and sulphides (Fig. 3c-g; Fig 4b). Secondary minerals in ocelli, such as zeolites and calcite, account for up to 2 vol.% of the rock. Porphyritic variety at the contact with encasing clays comprises anorthite + clinopyroxene + wollastonite in a groundmass of glass + Fe-rich clinopyroxene ± magnetite ± K-feldspar ± Fe-Al-spinel ± titanite ± sulphides. Wollastonite disappears close to the clay

wall-rock, with the rock becoming almost aphanitic. The contact with the pelite country-rock exhibits clinker breccia cemented by vesicular cryptocrystalline black glass. The suggested mineral formation sequence is as follows: (Al-spinel), anorthite → wollastonite → clinopyroxene → Fe-rich clinopyroxene → magnetite → glass → zeolites → "cement" minerals.

2.2.2. Late stage and contact facies

Contact facies are apparent at Colle Fabbri, showing the mechanical mixture and assimilation of clay country rocks. This produced a vesiculated brecciated facies which is a mixture of melilitic melt and clinkerised clay. The clinker fragment contains indialite, tridymite, glass, α-quartz relics plus felsic glass and Ti-magnetite. According to Stoppa and Sharygin [22] the formation of glassy clinker at the contact took place at 870–1000 °C. A late silicate-carbonate-sulphate association cemented the breccia and in particular the igneous rock near the contact. Mineralisation is pervasive, taking up all the free space and forming veins and concentric layered fillings in amygdales. This association is composed of carbonates (aragonite, calcite), sulphates (gypsum, barite), hydrated and/or hydroxylated silicates and sulphates (opal, ettringite, jennite, strätlingite, thaumasite, tobermorite), as well as various zeolites (chabazite, gismondine, phillipsite, willhendersonite). Further details can be found in Tables 1 and 2, and Sections 3.3 and 3.4.

3. Mineralogy

We limit the description to a) groundmass mesostasis, b) ocellar mineral occurrences, c) hydrothermal drusy crystals in amygdales and d) contact associated with igneous aqueous fluids. Late stage minerals are intended as groundmass or ocellar minerals, often in association with glass which crystallises in a temperature range of 680–720 °C, i.e. the glass inclusion incipient melting temperature [11–13, 23]. During this crystallisation the melt had an agpaitic index (A.I.) value close to 1 and a CaO content equal to that of alkalis. The appearance of the cuspidine enriched in hiortdahlite suggests an increase in melt alkali content. However, the rapid crystallisation of melilitolites with originally high Zr percentages appears to prevent Zr from forming its own Zr-mineral (hiortdahlite). Hence, Zr is scattered as isomorphic admixtures in cuspidine, götzenite, Zr-garnets and a poorly defined Ti-Zr-clinopyroxene. The appearance of the rhodesite group suggests melt evolution toward ultraperalkaline compo-
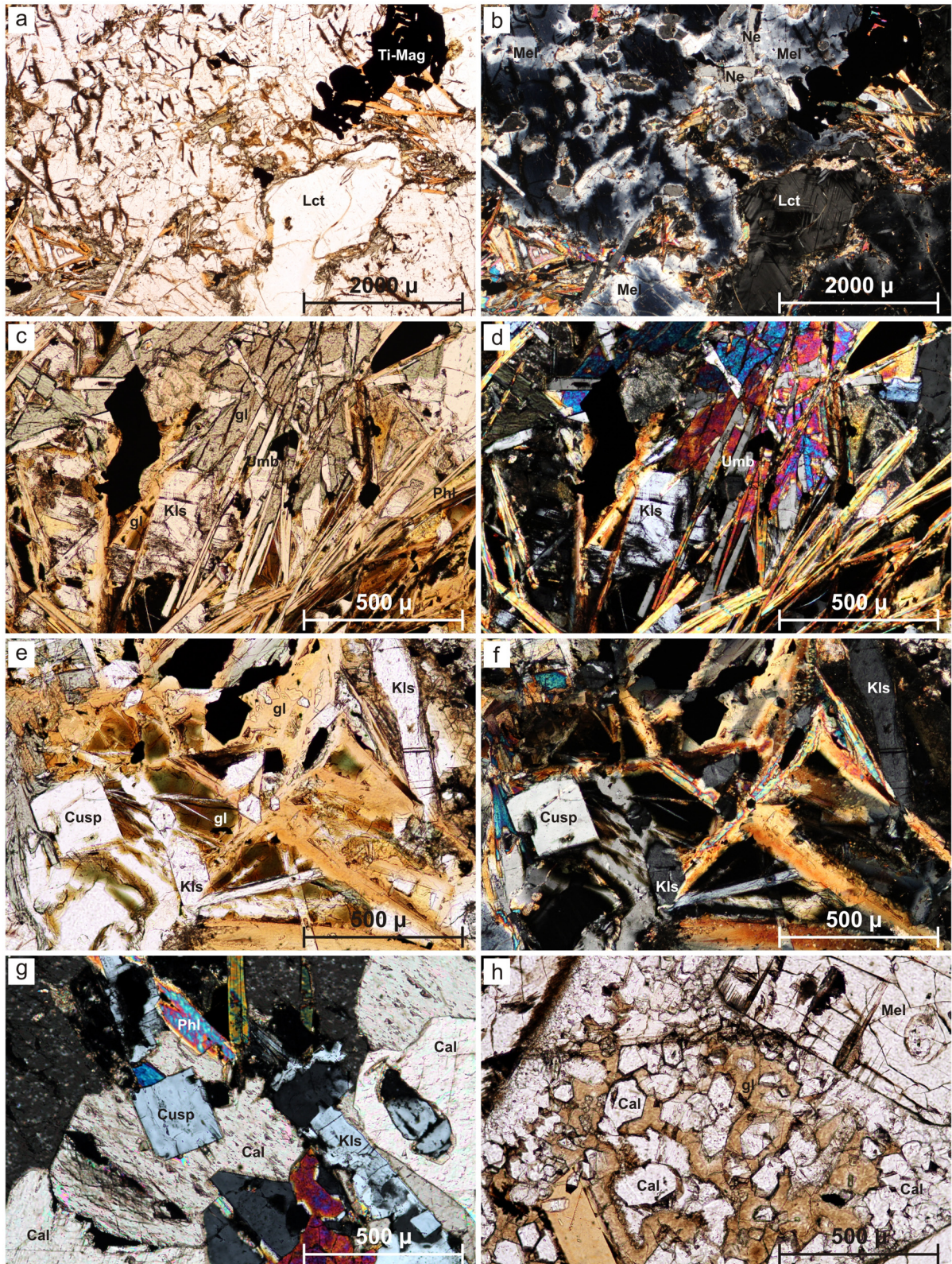
Figure 2. Transmitted parallel- and cross-polarised light photos of San Venanzo melilitolite in thin section. a-b- large melilite crystal showing blue anomalous polarising colour containing inclusions of nepheline, skeletal Ti-magnetite and leucite showing sector twinning. The intergranular component is green and brown glass, phlogopite and kalsilite, plus cuspidine, götzenite, apatite, calcite and other accessory phases; c-d- phlogopite, Ti-magnetite, kalsilite, umbrianite and green glass; e-f- kalsilite, cuspidine, götzenite, Ti-magnetite and apatite in green and brown glass; g- cuspidine, kalsilite and phlogopite in calcite (cross. polars); h- tabular melilite (top left) and calcite microphenocrystals hosted in brown glass (parallel polars). Abbreviations: Lct= leucite, Ne= nepheline, Me= melilite, Ti-Mag= Ti magnetite, Phl= phlogopite, Kls= kalsilite, Um= umbrianite, Cusp= cuspidine, Cal= calcite, gl= glass.
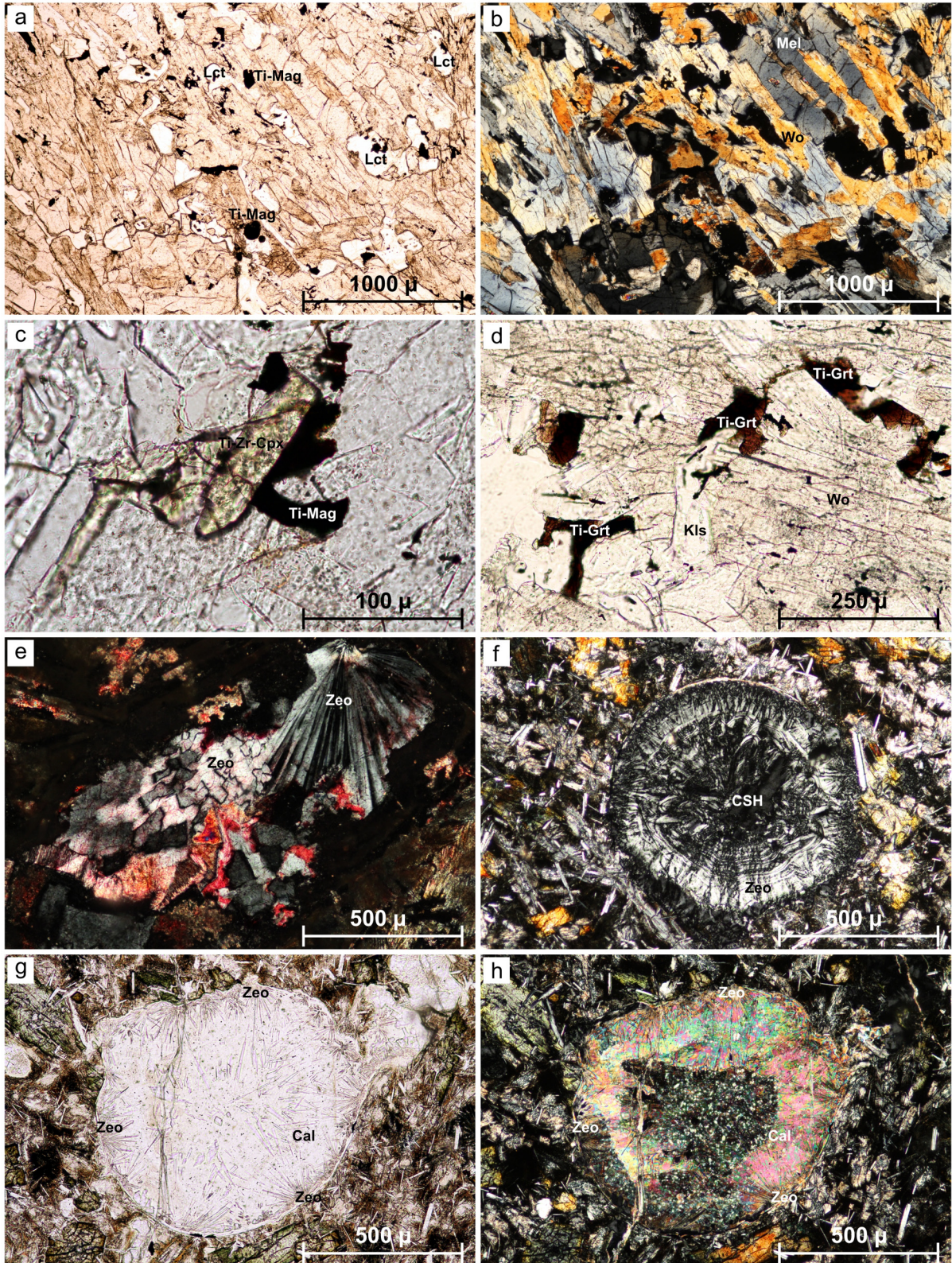
Figure 3. Transmitted parallel- and cross-polarised photos of Colle Fabbri melilitolite in thin section. a-b- melilite hosting wollastonite laths, with intergranular leucite and Ti-magnetite; c-intergranular Ti-Zr-clinopyroxene and Ti-magnetite; d- intergranular schorlomite and kalsilite; e- zeolites plus calcite stained with red alizarine (cross. polars); f- zeolite-CSH filled ocellus (cross. polars); g-h- zeolite plus calcite filled ocellus. Abbreviations as in Fig. 2 and Zeo= zeolite, Ti-Grt= Ti garnet, Ti-Zr-Cpx= Ti-Zr-clinopyroxene, Wo= wollastonite, CSH= calcium silicate hydrate.
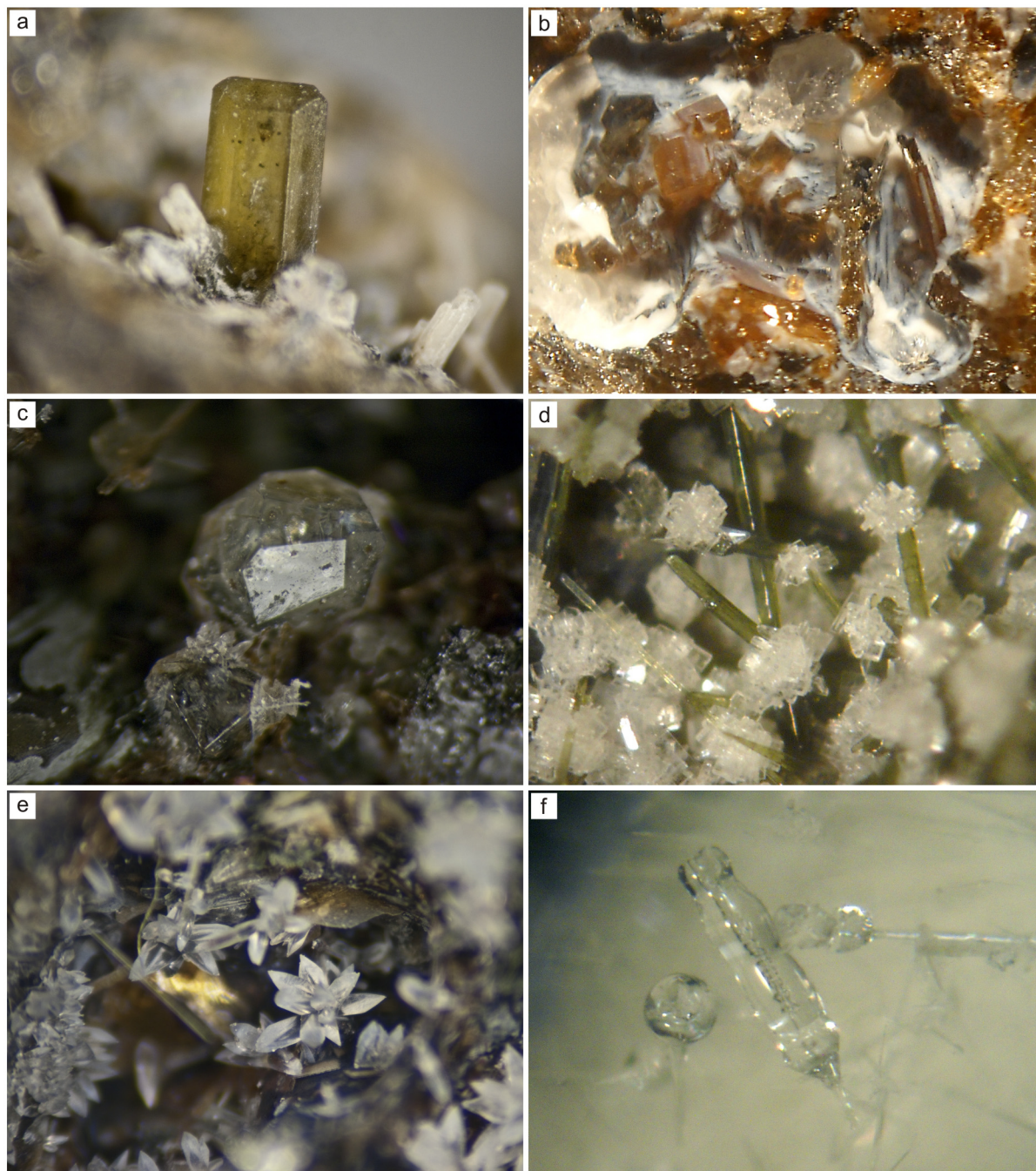
Figure 4. Reflected light microphotos of minerals from Colle Fabbri (CF) and San Venanazo (SV) melilitolites. a- forsterite (010) from SV (phot. L. Mattei); b- tabular honey melilite in zeolite-calcite amygdale from CF (phot. G. Bortolozzi); c- fresh euhedral leucite from SV (phot. L. Mattei); d- green clinopyroxene with willhendersonite aggregates from CF (phot. L. Bortolozzi); e-rhombohedral calcite from SV (phot. M. Luna); f- 'glassy' opal from CF (phot. G. Bortolozzi).

sitions during crystallisation. At this stage many metal–lic ores are deposited, such as vanadinite, westerveldite, bartonite etc. Hydrothermal minerals are largely associ–ated with igneous fluids circulating in the rocks after melt quenching. This aqueous system, probably rich in CO_2, is able to mobilise several elements such as Ba, K and Ca. These phases occur as well–shaped crystals in voids which also contain apophyllite and calcite. The walls of

Table 2. Synoptic table of mineral names with their formulas from San Venanzo and Colle Fabbri melilitolites, together with their respective temperature formation ranges [44, 45].

Group	Mineral	Chemical Formula/Empirica Formua	Cristalization temperature T(°)
Zr disilicates	Khibinskite	$K_2ZrSi_2O_7$	
	Ti-Zr-Garnet		
	Götzenite	$NaCa_6Ti(Si_2O_7)_2OF_3$	770-860°
	Cuspidine	$Ca_4(Si_2O_7)F_2$	770-860 °C
	Hiortdahline	$Na_4Ca_8Zr_2(Nb,Mn,Ti,Fe,Mg,Al)_2(Si_2O_7)_4O_3F_5$	
Rhodesite group	Umbrianite	$K_7Na_2Ca_2[Al_3Si_{10}O_{29}]F_2Cl_2$	
	Delhayelite	$K_7Na_3Ca_5Al_2Si_{14}O_{38}F_4C_{l2}$	
	Macdonaldite-like	$BaCa_4Si_{16}O_{36}(OH)_2 \times 10H_2O$	
Zeolite	Chabazite-Ca	$Ca_2Al_4Si_8O_{24} \times 13H_2O$	13-83°C
	Levyne-Ca	$Ca_3(Si_{12}A_{l6})O_{36} \times 18H_2O$	17-67 °C
	Willhendersonite	$KCa(Si_3Al_3)O_{12} \times 5H_2O$	13-83 °C
	Gismondine	$Ca_2(Si_4A_{l4})O_{16} \times 8H2O$	80-90 °C
	Phillipsite-Ca	$Ca_3(Si_{10}A_{l6})O_{32} \times 12H2O$	4-70 °C
	Ca-K zeolite (Merlinoite?)	$K_5Ca_2(Si_{23}A_{l9})O_{64} \times 24H_2O$	23-140 °C
Phyllosilicates	Apophyllite-(KF)	$(K,Na)Ca_4Si_8O_{20}(F,OH) \times 8H_2O$	
	Apophyllite-(KOH)		
Calcium Silicate Hydrate (CSH)	Tobermorite	$Ca_5Si_6O_{16}(OH)_2 \times nH_2O$	
	Jennite	$Ca_9Si_6O_{16}(OH)_{10} \times 6H_2O$	
	Afwillite	$Ca_3(SiO_4)(SiO_2(OH)_2) \times 2H_2O$	
Calcium Aluminum Silicate Hydrate (CASH)	Ettringite	$Ca_6A_{l2}(SO_4)_3(OH)_{12} \times 26H_2O$	100-350 °C
	Thaumasite	$Ca_3Si(OH)_6(SO_4)(CO_3) \times 12H_2O$	<100 °C
	Strätlingite	$Ca_2Al(Si,Al)_2O_2(OH)_{10} \times 2.25H_2O$	
	Vertumnite	$Ca_4Al_4Si_4O_6(OH)_{24} \times 3H_2O$	

the cavities hosting chabazite and phillipsite are lined in places by a very thin veneer of barite, Ba[SO₄]. The presence of the "cement" mineral associations supports the hypothesis that the formation of this mineral involves the effect of "sulphatising" fluids on carbonate–silicate rocks in a low pressure, low temperature (<100 °C) environment during a post–zeolitic stage of mineralisation. Many of these minerals are unstable in aqueous solutions and alter easily, with leaching of alkali cations and halogen anions accompanied by hydration. However, the CaAlSiO group remains stable during these transformations. Sections 3.1 to 3.4 elucidate the varying generation of mineral associations in San Venanzo and Colle Fabbri melilitolites and contact facies, with some comparison of those occurring in outcrops which are similar or regionally related. General mineralogical similarities and differences are addressed in Table 1, whilst genetic conditions are outlined in Table 2. Zeolites require the following special EMPA operating conditions: beam diameter of 1–2 μm, an accelerating voltage of 20 kV, a beam current of 15–20 nA and a counting time of 10 s for all elements. For Ba determination, standards were used for the quantification of Ba Sr– and Ba–rich synthetic silicate glasses and overlap corrections were performed for the following elements: Ba–Lα and Sr–Lα.

4. Zr-Ti-disilicates (khibinskite, cuspidine, hiortdahlite)

Khibinskite from olivine–hosted inclusions in Pian di Celle melilitolite [12] is slightly different from the Cupaello analogue [15, 24] in that it contains higher Fe^{2+}, Mg and Na, and lower K and Ti. To the authors' knowledge this occurrence of khibinskite is only the third recorded after that in the type locality, the Khibina alkaline massif [25]. ***Ti-Zr-garnet*** forms red–brown, irregularly shaped, zoned grains less than 100 μm in diameter in a leucite–bearing melilitolite groundmass (Fig. 3d). End–member calculation has revealed a solid solution of andradite–grossular–schorlomite, with less almandine. CaO is directly related to SiO_2. Colle Fabbri Ti–rich garnets contain up to 1.5 wt.% ZrO_2. The composition may change from schorlomite (TiO_2: 13–18 wt.%, core) to melanite (TiO_2: 10–12 wt.%, rim). A Ti–Zr–schorlomite is found in Polino carbonatite not far from Colle Fabbri [26]. ***Zr-Götzenite*** commonly occurs as colourless or pink–yellowish crystals confined to dark glass in the groundmass, but forms euhedra and crys–

tal clusters up to 3-5 mm in length in the voids. Götzenite occurs as slender, twinned euhedra or sheaf-like crystal aggregates with high interference colours under an optical microscope. It has been observed as overgrowth on cuspidine. In most cases, melt (or fluid) inclusions are associated with polycrystalline inclusions to form compound inclusions. Götzenite composition matches that of the götzenite from Mt. Shaheru and other localities [15, 27, 28]. Maximum abundances of REE_2O_3 and SrO in the götzenite are 5.4 and 1.2%wt. *Zr-Cuspidine* was found as crystal-phase inclusions in melilite and as discrete crystals in the ground mass of Pian di Celle and Colle Fabbri melilitolites (Fig. 2e). Cuspidine forms aggregates of spear-shaped crystals or individual crystals with a square cross-section of up to 0.25-0.5 mm, usually zoned (Fig. 2f). In the inclusions, cuspidine forms colourless, separated spear-shaped crystals or, more rarely, intergrowths of such crystals up to 20-40 μm in dimension. Sometimes the crystals show optical zoning with no sign of polysynthetic twinning. Microprobe analyses of the crystals reveal that the cuspidine displays both direct and inverse (sometimes rhythmic) zoning; component contents vary over a wide wt.% range as follows: CaO (58-44), ZrO_2 (0.2-10.6), Na_2O (0.5-3.6) and F (10.1-8.5). As a whole, Ca correlates positively with F and negatively with Zr and Na. All of these facts prove that Zr introduction into the cuspidine structure appears to result from isomorphism, suggesting miscibility between monoclinic cuspidine and triclinic hiortdahlite. Cuspidine from melilitolites contrasts with the cuspidine composition from high-temperature contact rocks in that it contains significant and variable ZrO_2 (0.2-11 wt.%) and Na_2O (0.5-4.5 wt.%), as well as Fe, Mn and Ti.

4.1. Rhodesite group (umbrianite, macdonaldite, hydrodelhayelite)

Umbrianite is usually localised in glass where it forms rectangular, lamellar, lath-shaped crystals occurring in sheaf-like clusters (Fig. 2c, d). Crystals and aggregates sometimes occur on the walls of cavities in melilitolite [29]. Umbrianite is orthorhombic, colourless and transparent in thin section. It has a vitreous lustre, with a hardness of ca 5 (Mohs scale). Cleavage is perfect on (010), and distinct on (100) and (001). Fracture is stepped to uneven across cleavage. The mineral is biaxial and not pleochroic. The simplified formula is $K_7Na_2Ca_2[Al_3Si_{10}O_{29}]F_2Cl_2$. Chemically, umbrianite is related to delhayelite belonging to the rhodesite mero-plesiotype series. Hydrated phases easily replace it; typically Ba-H_2O-rich (macdonaldite-like) or hydrodelhayelite-like minerals form a replacement rim. These phases occur in contact with potas-

sic minerals, i.e. kalsilite, leucite and rarely phlogopite. *Delhayelite* is colourless, generally similar to kalsilite optically, but sometimes showing cleavage parallel to elongation. This phase is partly pseudomorphed by macdonaldite, pale brown under an optical microscope and up to 10 μm across. The composition of delhayelite may be written as $K_4NaCa_2[Al_2Si_6O_{18}]F_2Cl$ [16]. *The macdonaldite-like* mineral occurs around the delhayelite-like phase but is chemically distinct from the latter. It is rich in BaO, H_2O, depleted in alkali and virtually (F, Cl)-free. The general formula of this mineral may be conventionally expressed as macdonaldite-like $HBa_{0.25}(Ca,Fe,Mg)_{0.75}Ca_2[Al_1Si_7O_{19}]_{0.5} \times 5H_2O$. Among double-layer silicates, macdonaldite is the most closely comparable with this mineral in terms of chemical composition [16].

4.2. Hydrothermal minerals (chabazite-(Ca) / levyne-Ca, phillipsite-(Ca), willhendersonite, merlinoite, thomsonite-(Ca), apophyllite)

Chabazite-Ca, $(Ca_{0.5},K,Na)_4[Al_4Si_8O_{24}] \times 12H_2O$ (Fig. 5a, e), was found co-existing with levyne-Ca, $(Ca_{0.5},Na,K)_6[(Si_6Al_{12}O_{36}] \times 17H_2O$, in the same crystal. The similarity of the two minerals' symmetries (R3) and a lattice parameter values explains their intergrowth. Crystals form colourless, transparent to milky-white, pseudocubic rhombohedra with typical [0001]-twinning, normally 300 μm in size. Chemical and X-ray analyses suggest that the investigated crystal is a combination of two intergrown crystals. In chabazite there is considerably more Ca, and considerably less K and especially Si, than in levyne. Taking into account both crystallographic and chemical data, another crystal from the same sample has been identified as levyne-Ca.

Willhendersonite, $KCa[Al3Si3O12] \times 6H_2O$, forms transparent, colourless or whitish, tabular crystals of up to 200 μm that form trellis-like twin intergrowths at right angles (Fig. 5b). SEM investigation revealed that the K and Ca contents are highly variable, with the Ca/K ratio always >1. Willhendersonite associated with other zeolites is even rarer, with only a few global occurrences reported thus far. Included among these are: 1) the San Venanzo and Cupaello twin occurrences [16, 30], which are regionally associated with the Colle Fabbri, Italy; 2) Styria, Austria [31]; and 3) the Eifel region, Germany [32–34].

Gismondine, $Ca[Al_2Si_2O_8] \times 4.5H_2O$, is an uncommon zeolite that has been found only in amygdales at Colle Fabbri [2]. Crystals show a pseudo-octahedral habit, are transparent, colourless to greyish in colour with a vitreous lustre and reach up to 1 mm across (Fig. 5c).
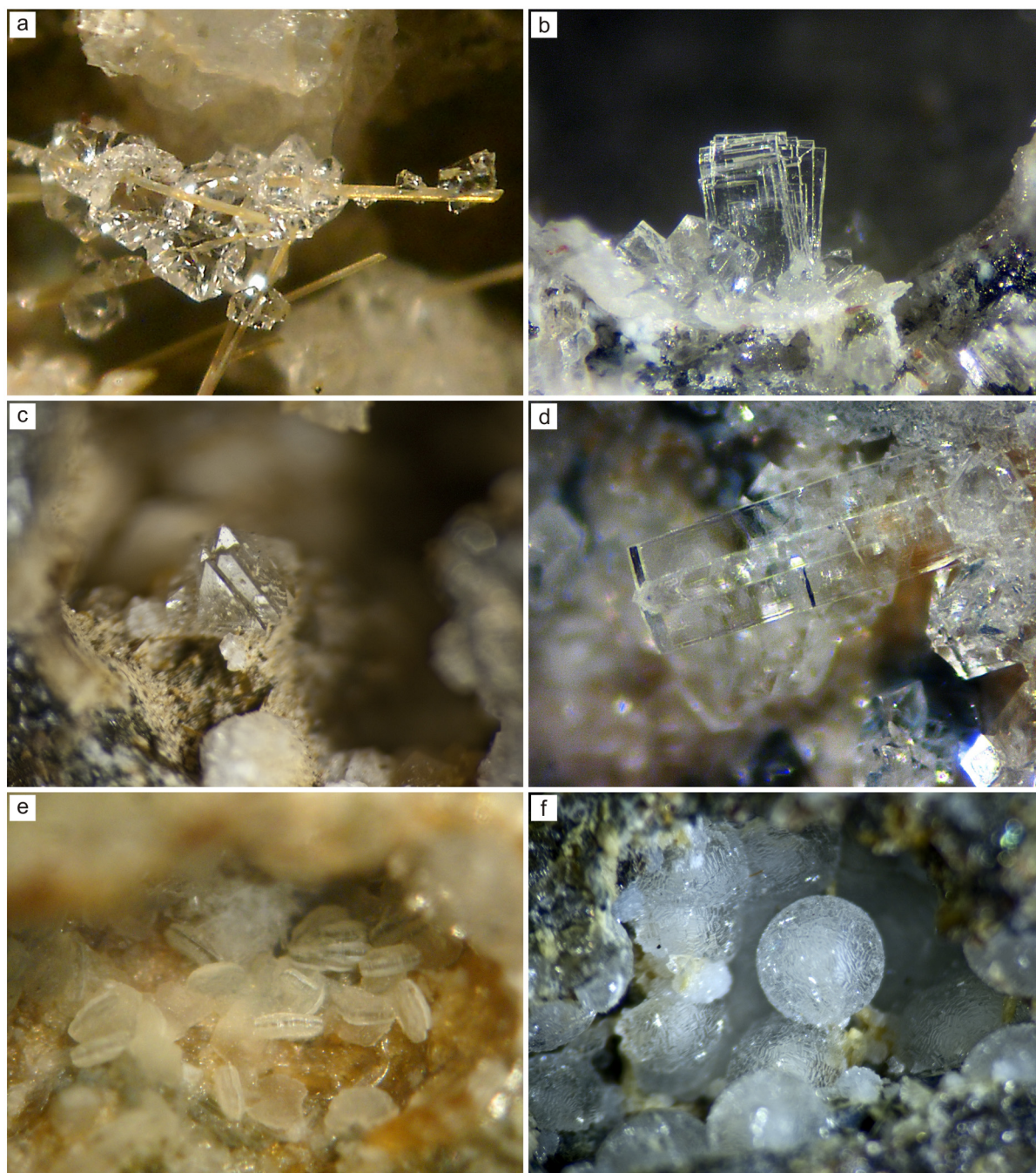
Figure 5. Reflected light microphotos of tentatively identified zeolites in CF and SV melilitolites. a- chabazite-(Ca) on fluorapatite from SV (phot. G. Bortolozzi); b- willhendersonite from CF (phot. L. Mattei); c- gismondine from SV (phot. M. Luna); d- phillipsite-(Ca) from CF (phot. L. Mattei); e- levyne-Ca/chabasie-(Ca) triplets from CF (phot. G. Bortolozzi); f- thomsonite-(Ca) from SV (phot. M. Luna).
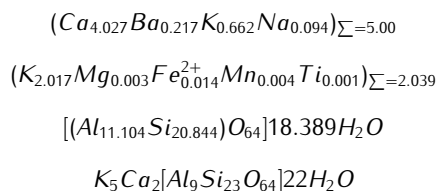
Phillipsite-Ca, $(K,Na,Ca_{0.5}, Ba_{0.5})_x$ $[Al_xSi_{16-x}O_{32}]×12H_2O$, is abundant in amygdales from both Colle Fabbri and San Venanzo [2, 29]. Its morphology is typically a short pseudo–orthorhombic prism with a–elongation, showing simple twinning or fourlings (Fig. 5d). Crystals are colourless and transparent with a vitreous lustre and are usually <1 mm across. The chemical composition of phillipsite includes a variable and sometimes high Ba content.

Ca–K zeolite (merlinoite?), $K_5Ca_2[Al_9Si_{23}O_{64}]×22H_2O$,

has been reported at Colle Fabbri [2] and is quoted in the literature as being orthorhombic with lattice parameters a = 14.116(7), b = 14.229(6) and c = 9.946(6) Å and space group Immm [35]. Although their lattice parameters may be similar, important dissimilarities are observed between merlinoite and the Ca–K zeolite. Whereas the former is centrosymmetrical with space group Immm, *Ca-K zeolite* seems non–centrosymmetrical (< E2-1 > 0.774, which is close to the expected value for non–centrosymmetrical structures, i.e. 0.736) with space group P2₁2₁2₁. When the chemical formula is considered and compared with the simplified one assigned to merlinoite:

$$(Ca_{4.027}Ba_{0.217}K_{0.662}Na_{0.094})_{\sum=5.00}$$

$$(K_{2.017}Mg_{0.003}Fe^{2+}_{0.014}Mn_{0.004}Ti_{0.001})_{\sum=2.039}$$

$$[(Al_{11.104}Si_{20.844})O_{64}]18.389H_2O$$

$$K_5Ca_2[Al_9Si_{23}O_{64}]22H_2O$$

We note that the bivalent (Ca, Ba) and monovalent (K, Na) cations present in Ca–K zeolite substitute for the K and Ca, respectively, in merlinoite.

Thomsonite-(Ca), $NaCa_2Al_5Si_5O_2 \times 6(H_2O)$, is uncommon and associated with chabazite–(Ca), phillipsite–(Ca), will-hendersonite and apophyllite in San Venanzo rocks [29], either as whitish globular aggregates formed by platy radiating crystals or as radiating, fan–shaped formations. Thomsonite is often found in alkaline mafic rocks, melilitite, nephelinite and phonolite, at sites including Hammerunterwiesenthal, Erzgebirge, Saxony, Germany and Děčín, Ústí Region, Bohemia, Czech Republic.

Apophyllite-(KF), $(K,Na)Ca_4Si_8O_{20}(F,OH) \times 8H_2O$, and *apophyllite*-(KOH) are frequently found associated with zeolites both at Colle fabbri and San Venanzo [2, 15]. They resemble zeolites and have rings, with the terminal non–bridging tetrahedral apexes of the four member rings pointing alternately up and down along the c–c tetrahedral axes. Adjoining layers are based on these rings. The rings oppose one another and form a Si–O–Ca–O–Si type of bond with the interim Ca-ions. This structure forms a void and, therefore, resembles a zeolite structure. The formula indicates that the dominant extra-framework cation is Ca. Assuming that Al and Si replace each other at the same site, the tetrahedral cations are in the ratio 2:3 = (Al,Si):S, also similar to ettringite.

4.3. Contact/metasomatic CSH (tobermorite, jennite, afwillite) and CASH (ettringite, thaumasite, strätlingite, vertumnite)

Tobermorite, $Ca_5Si_6O_{16}(OH)_2 \times 7H_2O$, occurs in white mammillary aggregates up to 500 *µm* across that have a vitreous lustre (Fig. 6a). Aggregates are composed of several individual crystals around 5-20 *µm* in diameter. Tobermorite occurs in two varieties: a 14 Å-tobermorite and an 11 Å-tobermorite, whose compositions differ in terms of their water content and periodicities along the silicate chains.

Jennite, $Ca_9Si_6O_{18}(OH)_6 \times 8H_2O$, appears as acicular crystals up to 0.5 mm along the b axis, usually grouped together to form tight bundles or radial aggregates. It has a whitish colour and vitreous lustre, often occurring in the innermost part of concentrically layered amygdales which contain a core of amorphous silica, microcrystalline calcite, aragonite and ettringite (Fig. 6b, d). Jennite is a rare mineral usually found in association with thaumasite in voids of the famous Kalyango carbonatite lava at Fort Portal, Uganda [36]. *Afwillite*, $Ca_3[SiO_3OH]_2 \times 2H_2O$, forms rare transparent columnar prisms (Fig. 6c) which are elongated and striated, and usually associated with either jennite (see above) or apophyllite, $(Na,K)Ca_4[(OH,F) \times (Si_4O_{10})_2] \times 8H_2O$, thaumasite and ettringite (see below). Interestingly, the type locality is the Dutoitspan and Wessels diamond mines in Kimberley, South Africa [37] Intensity statistics were used here to obtain indicative inform ation regarding inversion centre symmetry, although structural refinement may change this and is planned for the near future.

Ettringite, $Ca_6Al_2[(SO_4)_3(OH)_{12}] \times 26H_2O$, occurs in small globular aggregates with a pale yellowish colour and a matt lustre. The globules form the innermost part of concentrically layered amygdales that have internal voids. Substitution of Al for Si and partial replacement of $(SO_4)^{2-}$ with $(CO_3)^{2-}$ may lead to the formation of a solid solution between ettringite and thaumasite minerals, but, considering their dissimilar structure, is more likely to produce intergrowths of the two. Ettringite evolves to thaumasite or a poorly crystalline material when in contact with $CaCO_3$ and silica gel. In contrast to thaumasite, ettringite is very clearly identified under a scanning microscope and microprobe because of its transformation into metaettringite during the preparation of samples for analysis (carbon coating and vacuumisation). This is due to dehydroxylation under the condition T >50 °C [38]. Ettringite has also been found in Vulture carbonatites [39].

Thaumasite, $Ca_6Si_2[(CO_3)_2(SO_4)_2(OH)_{12}] \times 24H_2O$, occurs in felt-like aggregates of limpid, colourless–to–whitish crystals (Fig 6e). Parallel, elongated hexagonal prisms up to 1 mm along the c axis are common. It forms after microcrystalline calcite, tobermorite and amorphous silica. Microcrystalline aggregates of gypsum, $Ca[SO_4] \times 2H_2O$, and calcite are found as an alteration product after thaumasite. Three different minerals can in fact be described by the same chemical formula: thaumasite, jouravskite and
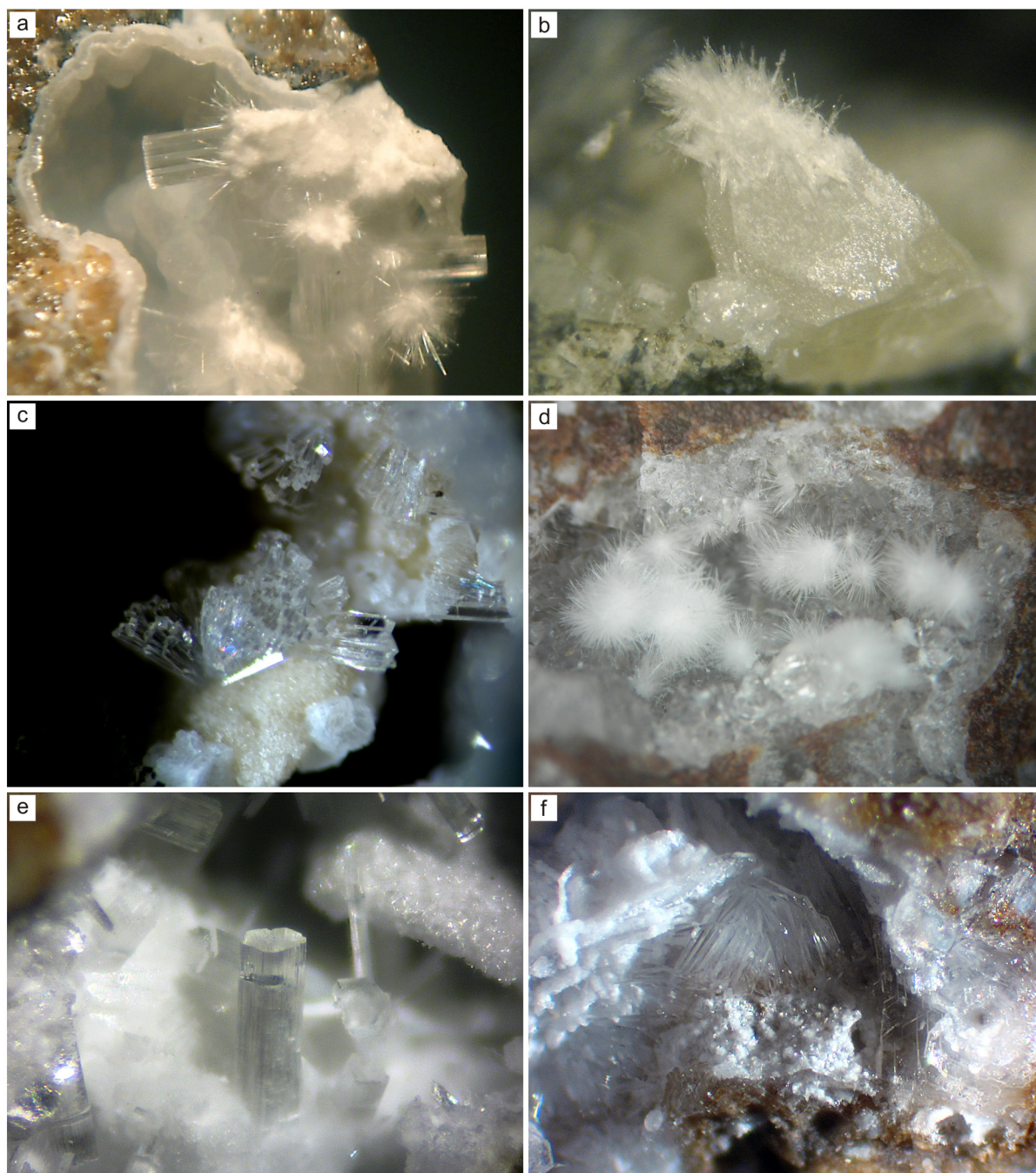
Figure 6. Reflected light microphotos of tentatively identified CSH and CASH minerals in CF melilitolite. a- ettringite on thaumasite plus tobermorite (phot. G. Bortolozzi); b- jennite on calcite (phot. G. Bortolozzi); c- afwillite (phot. M. Luna); d- ettringite (phot. L. Patrizi); e- thaumasite (phot. L. Mattei); f- strätlingite/vertumnite (phot. L. Mattei).

carraraite, given by $Ca_6X_4^{4+}(OH)_{12}(CO_3)_2(SO_4)_2] \times 24H_2O$, where X^{4+} = Si, Mn and Ge, respectively. The lack of Mn^{4+} identifies the mineral as thaumasite [2]. ***Strätlingite***, $Ca_2Al[(AlSi)O_2(OH)_{10}] \times 2.25H_2O$, and its polytype ver-tumnite, $(Na,K)Ca_4[(Si_4O_{10})_2(OH,F)] \times 8H_2O$, form whitish

hexagonal platy crystals up to 100 μm across, which are intergrown and possibly twinned (Fig. 6f). The crystal's chemical formula shows Ca^{2+} to be the dominant extraframework cation, as expected, even if the amount of water (7.95 H_2O p.f.u.) largely exceeds the 2.45 H_2O p.f.u.

confirmed by Galli and Passaglia [40]. The occurrence of this mineral in Colle Fabbri is one of the few found globally.

5.   Discussion

The exceptional rarity of such complex Zr–Ti silicates requires high alkali and silica activity in the crystallising liquid. Some are specific to peralkaline silicate melts, whereas others are found in associated carbonatites. A very similar case of Zr–Ti silicated speciation and distribution in peralkaline silicate rocks and carbonatites can be found in the Khibiny and Lovozero massifs in the Kola Peninsula, as well as other similar intrusions elsewhere [41]. All these minerals show a substantial degree of vicariance in Nb, Zr, Ti and Fe^{3+}. Fractionation of Hf and Ta with respect to Zr and Nb, a feature observed in the Italian alkaline suites and for some time interpreted as subduction imprinting, could be related to carbonate fractionation or separation. In addition, the role of volatiles including CO_2 and Fluorine should be considered. However, only microbeam mass–spectrometry, the application of which is far from the aim of the present paper, would guarantee a clear insight regarding mineral composition evolution in this rock suite. Relatively small amounts of compatible elements, Cr+Ni, and the virtual absence of olivine, suggest that melilitolites are differentiated with respect to associated melilitites and carbonatites. This implies that the crystallising liquid was residual with respect to an olivine melilitite melt. The melilitolites show extremely low SiO_2 and very high normative larnite content, likely produced by highly unstable CaO derived from carbonatite melt decomposition and the rapid formation of calcium silicate with a high Ca/Si ratio (rankinite, wollastonite, cuspidine). As melilitolites crystallise, a sharp change in physical chemical conditions occurs, passing from an A.I. (Agpaitic Index) value close to 1 and a CaO content equal to that of alkalis to peralkaline conditions (A.I. >1.2). The residual glass inclusions within melilite and the interstitial glass of the rock are ultra–agpaitic (A.I. ±10) and alkalis dominate over CaO. Cuspidine and götzenite crystallise just before kalsilite and nepheline. The appearance of a cuspidine external rim enriched in hiortdahlite molar compounds suggests an increase in melt alkali content. The rapid crystallisation of melilitolites with originally high Zr percentages appears to prevent Zr from forming its own Zr–mineral (hiortdahlite). Hence, Zr is scattered as isomorphic admixtures in cuspidine and götzenite. In summary, the originally high concentrations of CaO, F, Zr and alkalis, the deficit of SiO_2 in the melilitolite parental magma, as well as the agpaitic trend of

magma evolution, all contributed to cuspidine formation at T >770–860 °C and P <1 kbar. After carbonatite extraction the silicate liquid fraction moved on to a strong peralkaline, phonolitic trend, high in Zr, F, Ba and Cl, and low in Ca, where khibinskite crystallisation was favoured. The main difference between the San Venanzo and Colle Fabbri melilitolites is derived from alkali content dilution and the addition of aluminium via melt/country–rock assimilation/metasomatic/fluid release phenomena at Colle Fabbri. Clear zonation of Colle Fabbri melilitolite shows that Zr–Ti silicates are confined to the inner part of the stock and are not found in the contact facies. High CO_2 fugacity may lead to the depletion of LREEs and of some HFSEs. Slow magma emplacement at subvolcanic level would have triggered this process, favouring both the concentration of fluids along the eruptive fracture and hydrothermal mineralisation. CO_2–rich hydrothermal fluids of these stages mobilise hydromagmatophile elements such as K and Ba, with other large–ion lithophile elements, OH/H_2O ratios and a high Ca content all features likely linked to hyperalkaline steam–heated, juvenile and/or connate fluids producing complex secondary mineral crystallisation at low temperatures, such as 1) calcite and tobermorite; and 2) zeolites and strätlingite. The same is the case for the following "cement" minerals such as 1) thaumasite, ettringite, jennite, calcite (drusy) and aragonite (microcrystalline); and 2) barite and gypsum. Silica–calcite reaction in the presence of water/steam or even at temperatures lower than 100 °C can produce sulphate carbonate–silicate reaction with juvenile–connate water during a post–zeolitic "cement" stage. A decrease in the Ca/Si ratio in the solid phase converts Ca–Ba–zeolites into CSH and CASH, which then become the predominant crystallising phases. Hydroxylated silicate sulphate–carbonates can be generated under transient chemical conditions [42, 43]. Oldhamite is an ephemeral mineral which may form as a high–temperature phase that rapidly hydrates to CSH and CASH under alkaline conditions. This phase is followed by the alteration of previous minerals, mostly at near room temperature.

6.   Conclusions

Colle Fabbri and San Venanzo have a similar genetic environment, as observed in a few other young K–rich peralkaline volcanic rocks. Large–ion lithophile elements such as K, Sr and Ba are distinctively concentrated in the melilitolite minerals as well as in kamafugitic melts. The progressive changes in the mineralogy suggest deposition within a cooling system following the possible sequence: <1250 °C crystallisation of melilitolite melt – <1000 °C car-

bonate immiscibility and groundmass mesostasis moving towards an ultraperalkaline composition – <400 °C hydrothermal and metasomatic reaction of minerals – <300 °C zeolite formation – <100 °C weathering of previous minerals and "cement" mineral formation. The formation of the rare mineral assemblage of the Pian di Celle melilitolite reflects the abrupt change in composition of the crystallising liquid. Zr-Ti phase minerals rapidly precipitated in the groundmass and in the ocelli, which are believed to represent immiscible carbonatitic liquid. Increasing Zr and Ti content in minerals occurred in parallel to increasing A.I. and the quenching of ultra-peralkaline glasses (A.I. >10). The ultra-peralkaline character of the residual liquid was also responsible for the appearance of delhayelite-macdonaldite minerals and K-Cl-sulphide, while the change in redox conditions after the separation of CO_2 from the silicate liquid fraction was probably responsible for the appearance of sulphides (mainly FeS) and arsenides instead of Fe-oxides. These fluids were very rich in CO_2, a component which is always highly abundant in carbonatite-related magmas. A notable difference is the buffering operated by clay assimilation at Colle Fabbri, which prevented or limited the formation of ultra-peralkaline residual liquid (glass) and, consequently, the appearance of extreme Zr-Ti-disilicates, even if some peculiar higher temperature phases, Zr-schorlomite, Ti-cpx and perovskite are also present as observed in carbonatitic rocks in Italy and elsewhere. Passage to non-igneous temperatures is marked by metastable reactions and zeolite formation. It is apparent that CSH-CASH are the dominant products forming via the circulation of low temperature fluids. Sulphates and hydrated and/or hydroxylated silicate sulphate- carbonates of Colle Fabbri are rare in silicate igneous rocks, and seem to be restricted to carbonated melts such as carbonatites, kimberlites and kamafugites.

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