

Petrological and geochemical constraints on the origin of apatite ores from Mesozoic alkaline intrusive complexes, Central High-Atlas, Morocco

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- Petrological and geochemical constraints on the origin of apatite
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18 Abstract

Five main apatite deposits from the Moroccan Central High-Atlas —including 19 Anemzi, Tirrhist-Inouzane, Tassent, Ait-Daoud-Toumliline and Tasraft- have been 20 investigated through integrated field, petrographic, mineralogical, and geochemical 21 studies. The apatite ore occurs as veins, few mm to several cm thick, spatially 22 associated with syenite-quartz monzonite (dominant) to monzodiorite-gabbrodiorite 23 bodies emplaced during the Atlas Jurassic-Cretaceous alkaline magmatic event. Gem-24 quality apatite crystals, up to 15 cm in size, are associated with albite, clinopyroxene 25 26 (hedenbergite-augite-diopside), amphibole (hornblende-edenite-actinolite), K-feldspar, quartz, magnetite, titanite, epidote, prehnite, and calcite. Two types of apatite have 27 28 been distinguished according to their halogen contents: F-rich and Cl-rich apatites. Both types are enriched in REE (up to 2 wt.% ΣREE), and have major and trace element 29 30 contents consistent with a magmatic origin, corroborated by the chemical similarity with 31 accessory apatite in the host alkaline intrusions, as well as with other reference igneous apatites. However, hydrothermal fluids percolating through country sedimentary rocks 32 33 were also involved, as indicated by the striking Na enrichment observed in the CI-rich apatites, likely inherited from Triassic evaporites, showing close spatial relationships 34 with the alkaline intrusions. These fluids would also account for pervasive Na-35 metasomatism of alkaline magmatic rocks, as observed in the wall rocks of the apatite 36 veins. 37

Keywords: Moroccan Central High-Atlas, alkaline magmatic event, vein-type apatite
 ores, F-rich and Cl-rich apatites, magmatic origin/hydrothermal fluids.

41 **1. Introduction**

42 Apatite is the most ubiguitous accessory phosphorus(P)-bearing mineral found in 43 sedimentary, igneous and metamorphic rocks. It is also sometimes a major rock-forming mineral in some peculiar rock types: e.g. sedimentary phosphorites and some igneous 44 45 rocks of alkaline, carbonatitic and anorthositic affinities (e.g., McConnell 1973; Glenn et al., 1994; Dymek and Owens 2001; Martin and Rakovan, 2013; Duchesne and Liégeois, 46 2015; Pufahl and Groa et al., 2017). Apatite is the only major potential resource of P 47 48 used in the manufacturing of e.g., nitrogen-phosphorus-potassium (NPK) fertilizers, animal feed supplements, ceramics, pharmaceuticals, textiles and batteries. The 49 sedimentary phosphorites make the largest contribution to the world production of 50 phosphate, whereas igneous apatite rocks account for only ~ 10 % (e.g., Jasinski, 2016; 51 Pufahl and Groa et al., 2017). The igneous phosphate ores are nevertheless 52 economically valuable since they provide high quality phosphate concentrates with low 53 contents of unwanted contaminants such as Cd, As, Pb, Si and Al, and they are rich in 54 Rare Earth Elements (REE) (e.g., Webster and Piccoli, 2015; Chakhmouradian et al 55 2017). In terms of world resources, Morocco is the largest holder and producer of 56 sedimentary phosphates, with reserves estimated to represent about ~ 76 % of world 57 reserves (e.g., Jasinski, 2016, 2019; Pufahl and Groa et al., 2017; www.ocpgroup.ma). 58 59 However, Morocco also bears igneous phosphate ores, especially in the High-Atlas mountain range. Over the last two decades, gem-quality apatite crystals well-60 appreciated by mineral collectors and known as "Moroccan High-Atlas Imilchil-Anemzi 61 apatite" were made available on the international mineral market (e.g., 62 https://www.minfind.com/mineral-569173.html; https://www.mchminerals.com/fine-63

mineral-specimens/apatite-morocco; Rakovan, 2015). Despite their economic and 64 scientific interests, only one recent study (Dumańska-Słowik et al., 2018) was devoted 65 to the Anemzi apatite, chiefly dealing with organic inclusions, and a detailed 66 characterization of the apatite ores remains to be done. This paper provides the first 67 description of the main apatite deposits in the High-Atlas region. We carried out an 68 69 exhaustive petrographic, mineralogical, and geochemical study (major, volatile, and trace elements) of the apatites and associated minerals, and of the host lithologies. 70 These data are used to identify suitable sources for the phosphate mineralization. 71

72 2. Geological setting

73 The High-Atlas (up to 4000 m elevation) constitutes a typical intra-continental Alpine orogen, forming a thrust chain resulting from the Africa–Eurasia convergence. Its 74 growth started during the early Mesozoic with the reactivation of Pangea paleo-faults 75 which delimited subsidence sedimentary basins, leading to the Atlantic Ocean opening 76 at the NW Africa margin (e.g., Stampfli and Borel, 2002; Piqué et al., 2002; Teixell et al., 77 2003; Laville et al., 2004; Frizon de Lamotte et al., 2008, 2009; Domènech et al., 2015). 78 This chain includes several segments, such as the Western, Central and Eastern High-79 Atlas (Fig. 1a). In contrast with the two other segments, the Central High-Atlas 80 corresponds to the deepest part of the orogen (Fig. 1b; e.g., Teixell et al., 2003; Frizon 81 de Lamotte et al., 2008, 2009; Gouiza et al., 2010; Michard et al., 2011). Several works 82 have described the lithostratigraphical sequence of this belt (Fig. 1b-c; Charrière et al., 83 2005, 2009; Haddoumi et al., 2002, 2010; Ettaki et al., 2007; Frizon de Lamotte et al., 84 2008, 2009; Cavin et al., 2010; Saura et al., 2014; Charrière and Haddoumi, 2016, 85 2017; Cavallina et al., 2018). The first Mesozoic sediments are Triassic red argilites and 86

evaporites (mostly halite and gypsum) forming more than 1000 m-thick series which 87 deposited within subsident basins and which cover unconformably a leveled 88 Precambrian-Paleozoic basement (e.g., Du Dresnay, 1987; Piqué et al., 2002; Eddif et 89 al., 2007; Ouabid et al., 2017, 2020; Boukerrou et al., 2018; Karaoui et al., 2021). These 90 deposits are generally interbedded with tholeiitic lava flows linking to the Central Atlantic 91 Magmatic Province (e.g., Marzoli et al., 2019 and references therein). Subsequently, a 92 regional marine transgression led to the deposit of a series of Early Jurassic carbonates 93 (mostly limestones and marls). During the Middle Jurassic and Lower Cretaceous, 94 conformable red beds of continental sandstone settled, indicating the filling of basins 95 and a marine regression. Overall, these post-rift basins were controlled by sinistral 96 strike-slip faults, and separated by Triassic diapiric anticlinal ridges with dominant NE 97 trending (Fig. 1b-c; e.g., Laville and Pique, 1992; Saura et al., 2014). In the Middle 98 Cretaceous, a new marine carbonated platform sets up (e.g., Froitzheim et al. 1988; 99 Cavallina et al., 2018 and references therein), and at the end of the Cretaceous, the 100 sediments consist of terrigenous red beds, expressing the early manifestation of the 101 Alpine orogeny (e.g., Laville et al. 1977; Froitzheim et al. 1988; Ettachfini and Andreu, 102 103 2004; Ettachfini et al., 2005; Michard et al., 2011; Cavallina et al., 2018). The Central High-Atlas Mesozoic ridges are often unconformably overlain by Paleocene non-marine 104 red bed formation which draws the synclinal geometries attributed to Late 105 106 Cretaceous–Cenozoic shortening and halokinesis (Fig. 1c; e.g., Charriere et al., 2009; Michard et al., 2011). The famous Cenozoic alkaline-carbonatite magmatic episode (~ 107 108 45–35 Ma) that occurred at NW Central High-Atlas Tamazight area (Fig. 1b) coincides

with the African–European collisional event (e.g., Bouabdli et al., 1988; Bernard-Griffiths
et al., 1991; Bouabdellah et al., 2010).

In addition, the core of the Central High-Atlas anticlinal ridges is formed by an 111 important Jurassic-Cretaceous alkaline to transitional magmatism between ~ 165 Ma 112 and ~ 125 Ma (Fig. 1b-c; e.g., Hailwood and Mitchell 1971; Westphal et al., 1979; 113 Beraâouz and Bonin, 1993; Rahimi et al. 1997; Armando, 1999; Haddoumi et al., 2010; 114 Michard et al., 2011, 2013; Bensalah et al., 2013). This magmatism occurs as 115 numerous dykes, sills and laccoliths, either intrusive along faults and narrow anticlinal 116 ridges or intercalated in the thick Mesozoic sedimentary series (Fig. 1b-c; e.g., 117 Armando, 1999; Teixell et al., 2003). Basaltic lava flows within wide synclines are also 118 reported (e.g., Guezal et al., 2011; Bensalah et al., 2013; Michard et al., 2013). The 119 magma emplacement was mainly controlled by faults coeval with halokinetic tectonic 120 and moderate syn-schistous deformation, might link to the widespread exhumation 121 122 resulting from the orogen during the Upper Jurassic-Early Cretaceous (e.g., Laville and Pique, 1992; Frizon de Lamotte et al., 2008, 2009; Michard et al., 2011; Saura et al., 123 124 2014; Torres-Lopez et al., 2016; Essaifi and Zayane, 2018). Metamorphic aureole around the intrusions is almost absent at the contact with the country sedimentary 125 rocks, which are mostly faulted (e.g., Fig. 1b-c). The tectonic boundaries are mostly 126 vertical/sub-vertical faults marked by brecciated formation composed of fragments of 127 igneous intrusive and carbonate rocks. However, some rare normal contacts between 128 the intrusions and the sedimentary sequence are observed with chilled marginal 129 magmatic rocks with carbonates recrystallization that occurred at about 300-500 °C 130 (Lhachmi, 1992, Armando, 1999; Lhachmi et al., 2001; Essaifi and Zayane, 2018). The 131

intrusive complexes include almost all terms of alkaline magma differentiation series 132 (e.g., Armando, 1999; Lhachmi et al., 2001; Zayane et al., 2002; Essaifi and Zayane, 133 2018). The intrusions are made up to 60–70% of troctolites, gabbros, and 134 monzogabbros, while the remaining volume is represented by differentiated rocks 135 (mostly monzonites and syenites). Depside the fragmentation of the intrusive bodies 136 137 into several blocks which hampers to infer more information about the primary relationships, the differentiated unit seems to be intrusive into the mafic unit (e.g., 138 Armando, 1999; Lhachmi et al., 2001; Essaifi and Zayane, 2018). The evolution of the 139 magma sequence from mafic to felsic members would be mainly linked to fractional 140 crystallization, whereas crustal contamination during the magma ascent cannot be 141 excluded (e.g., Armando, 1999; Lhachmi et al., 2001, Zayane et al., 2002; Essaifi and 142 Zayane, 2018). The magmatism is interpreted to be formed in a transpressional tectonic 143 setting where the Central High-Atlas experienced a significant uplift and orogenesis 144 during the Jurassic (e.g., Laville and Pique, 1992), or in an asthenosphere mantle 145 upwelling context beneath the orogen with partial melting of enriched upper mantle 146 components without significant crustal extension (e.g., Frizon de Lamotte et al., 2009; 147 148 Michard et al., 2013; Essaifi and Zayane, 2018). From our field observations, the major apatite deposits of the Moroccan Central High-Atlas --enclosing Anemzi, Tirrhist-149 150 Inougzane, Tassent-Tarstaft, Tarstaft, and Ait Daoud-Toumliline deposits, Figs. 1b, c-151 are always spatially associated to these Jurassic-Cretaceous alkaline intrusions. The apatite ores form mm- to several cm-thick veins without any preferential trending and 152 the current mining is done only in an artisanal way and the only economic opportunities 153 154 are for mineral collectors. Unfortunately, the limited extension of the exposed apatite

veins hides more information about the lateral extensions, but the scraping of the 155 apatite ores generated by the mineral collectors could vary between 2 and 40 m long. 156 These apatite-producing localities are isolated and less abundant. The contacts 157 between the apatite veins and their host magmatic rocks are mostly sharp without any 158 clear zonation and the mineralogical compositions of the vein-type apatite ores and its 159 160 host rocks from different localities are slightly variable, whereas the main components are always alkali feldspars, pyroxene, amphibole, quartz, prehnite, calcite, magnetite, 161 epidote, and titanite (detail below). 162

3. Sampling and analytical methods

The five Moroccan Central High-Atlas apatite deposits cited above (Fig. 1) were 164 investigated. For each deposit, we sampled apatite mineralized veins and their direct 165 country magmatic rocks (see Table 1). Apatite crystals have been separated by hand, 166 included in epoxy mounts and polished. These apatites, the gangue-forming minerals, 167 and the country rocks were also studied in polished thin-sections. For petrographical 168 observations, we used standard microscope Leica DM2700P in the Geo-AnalyticalLab 169 of Geology and Sustainable Mining Department, Mohammed VI Polytechnic University 170 (UM6P, Benguerir, Morocco). 171

Seven representative samples of the magmatic rocks hosting the apatite mineralization veins were selected for whole-rock geochemical analyses of major elements and some trace elements performed at the Instituto Andaluz de Ciencias de la Tierra (IACT-CSIC, Granada, Spain). The samples include Anemzi AP45 and AP54, Tirrhist-Inouzane AP10, Ait Daoud-Toumliline AP08 and AP09, Tassent AP27 and

Tasraft AP61 (Table 1). Rock powders were obtained using a jaw crusher and an agate 177 ring mill. Loss on ignition (L.O.I) was determined by drying the samples at 900°C, and 178 ranges from 0.07 to 5.86 wt.%. (CI, Cr, Co, Ni, Cu, Zn, Ga, Zr, Sr, Y, Nb) The analyses 179 were performed using a sequential spectrometer Bruker AXS S4 Pioneer equipped with 180 three analyzers (LiF200, OVO-55, PET). For X-ray fluorescence (XRF) major element, 181 182 Cr, Ni, Zr, Sr and Y analyses, rock powders (c. 1 g) were weighed with di-lithium tetraborate flux, and then the mixture was fused at 1000 °C for 15 min. Within run 183 precision (% RSD), measured by repeated analyses of USGS BHVO-2 and AGV-2 184 reference materials as external standards was better than 1.5% for all the elements 185 except P (2.7%) (Varas-Reus et al., 2018). The other minor elements and SO₃ were 186 analysed in pressed powder pellets in an independent calibration. The analyses of 187 certified reference materials (BIR-1) have been used as external standard and the 188 accuracies are <5% for major elements and <11% for minor elements. 189

190 In situ analyzes of major and minor elements for minerals were carried out using the Cameca SX100 Electron Microprobe at the Geosciences Montpellier (Montpellier, 191 192 France). Analyses were obtained using a beam size of 30–40 µm for apatite and 5 µm for the minerals of gangue and country rocks, an accelerating voltage of 15 kV and a 193 probe current of 20 nA. The counting time was fixed at 20 s for major elements and 40 s 194 for F, CI, and S. Combination of natural —including fluorapatite (F, P), chlorapatite (CI), 195 196 orthoclase (K), albite (Al, Na), wollastonite (Si, Ca), forsterite (Mg, Fe), baryte (S), rhodochrosite (Mn)— and synthetic (TiO₂ and Cr₂O₃) standards are used for the 197 calibrations. The apatite and the associated pyroxene and amphibole were analyzed for 198 trace elements using the Laser Ablation Coupled Plasma-Mass Spectrometry (LA-ICP-199

MS) at Geosciences Montpellier (AETE platform, OSU-OREME). Signals were acquired 200 in Time Resolved Acquisition. Each analysis consisted of a pre-ablation pulse of 5 s and 201 2 min for the blank and 1 min for measurement. The laser was fired employing an 202 energy density of 15 J/cm2 at a frequency of 5 Hz and using a spot size of 50 µm. 203 Reference material NIST612 glass (Pearce et al., 1997) was used as external standard 204 205 and CaO and SiO₂ contents determined by electron probe were used as internal standards. Data were processed using the GLITTER software (Griffin et al., 2008). LA-206 ICP-MS data accuracy and precision were assessed using the obtained results from the 207 BIR-1G glass and show good agreement with published values for this international 208 reference material (Gao et al., 2002; Jochum et al., 2005, 2016). 209

210 **4. Petrography**

211 4.1. Anemzi

In the Anemzi veins, the apatites (~ 10–30 vol.% of the vein) occur as hexagonal 212 prisms with variable sizes that can reach more than 6 cm length and more than 3 cm 213 width (Fig. 2). They are present in two different types of gangue (Fig. 2a-b). The first 214 one is white in color and it mainly consists of calcite, plagioclase (albite), K-feldspar, 215 magnetite, and quartz (Figs. 2c-d). Calcite occurs as medium- to fine subhedral to 216 217 anhedral crystals (~ 0.1–0.8 mm in size) and is the dominant gangue-forming mineral (up to 40 vol.%), filling the spaces between the other minerals. Albite and K-feldspar are 218 abundant (up to 25 vol.%) euhedral crystals (~ 0.2–1 cm in size) with sericitized cores 219 and fresh rims. Magnetite is omnipresent and occurs as red-brownish euhedral 220 prismatic to anhedral crystals up to 0.5 cm in size. Quartz is less abundant, euhedral to 221

subhedral, and small in size (< 0.5 mm). The second gangue type is dark, and it is 222 made almost exclusively of needle-shaped amphibole (mostly hornblende) with 223 subordinate chlorite as a product of amphibole transformation (Figs. 2b, e). The most 224 beautiful Moroccan apatite gems are extracted from veins within white gangue: they are 225 characterized by their perfect euhedral habit, transparency, green-yellow color and 226 227 glassy luster (Fig. 2a). In contrast, the apatites associated with dark gangue are cloudy crystals, pale green to grey in color, with little or no luster and enclosed many euhedral 228 needles of amphibole similar to those present in the matrix veins (Figs. 2b, e). 229

The Anemzi apatite veins are mainly hosted in medium- to coarse-grained mesocratic to leucocratic magmatic rock which consists of 40 to 60 vol.% of albitic plagioclase (An < 10 %), 20–25 vol.% of K-feldspar and 2–8 vol.% of quartz (Fig. 2c). Chlorite and Fe-oxides are omnipresent: they result from the complete transformation of ferromagnesian minerals (i.e., pyroxene, amphibole) which are no longer present in the rock. Accessory minerals include rutile, apatite, and zircon. Calcite is also observed as secondary mineral phase.

4.2. Tirrhist-Inouzane

The Tirrhist-Inouzane veins provide gem-quality apatites (up to 15 vol.%) transparency and luster with similar color than apatites from the Anemzi region (Figs. 3a, b). The size of apatite crystals is variable but can reach 3 cm length. The gangue consists of clinopyroxene, albite, epidote, quartz, K-feldspar, and subordinate chlorite (Fig. 3c–d). Clinopyroxene occurs as euhedral to subhedral crystals (up to 1 cm in size), forming the main gangue component (up to 35 vol.%). Zonation of some clinopyroxene

crystals is highlighted by the alternance of dark and light green domains. Epidote is 244 abundant (up to 20 vol.%) and it appears as subhedral to euhedral crystals (~ 0.2–1 cm 245 in size). Albite (dominant), quartz and K-feldspar (rare) represent around 30 vol.% and 246 occur as medium- to fine subhedral to anhedral crystals (~ 0.1–1 mm in size), filling the 247 interstices among clinopyroxene, epidote, and apatite. These apatite veins crosscut 248 249 medium-grained to pegmatitic leucocratic magmatic rock rich in albitic plagioclase (up to 85 vol.%) (Figs. 3a, e, f) and also contain clinopyroxene (5–10 vol.%), and subordinate 250 (< 5 vol.%) quartz and K-feldspar. Magnetite (sometimes with ilmenite exsolutions), 251 stilpnomelane, apatite and zircon are also observed. Chlorite, epidote and sericite occur 252 as secondary mineral assemblage. 253

254 4.3. Tassent

The apatites (~ 10–20 vol.%) associated with the Tassent veins are elongated crystals up to 15 cm length and 4 cm wide (Figs. 4a, b). They are pale yellow to pale green with an opalescent luster. The gangue mineral assemblage consists mainly of prehnite and quartz (~ 60 vol.%), plus clinopyroxene and epidote (Figs. 4c, d). Prehnite and quartz occur as euhedral to anhedral crystals (up to 3 mm in size). Clinopyroxene appears as euhedral to subhedral destabilized crystals (up to 1 cm in size). Epidote is occasionally observed as yellow-greenish euhedral crystals (< 0.5 mm in size).

The apatite veins are hosted by medium-grained mesocratic to leucocratic magmatic rocks (Figs. 4a, e), which consists of albitic plagioclase (up to 60–70 vol.%), amphibole (15–20 vol.%), quartz (5–10 vol.%) and subordinate (< 5 vol.%) K-feldspar

and clinopyroxene. Titanite, apatite and zircon are the main accessory minerals, and
epidote and chlorite occur as alteration products.

267 4.4. Ait Daoud-Toumliline

The apatites (10–20 vol.%) from the Ait Daoud Toumliline veins are gem-quality 268 dark green, with moderate vitreous luster and characterized by an abundance of 269 amphibole inclusions (Figs. 5a to 5c). Their size can reach 3 cm. They are found in a 270 gangue composed mainly of amphibole, prehnite, guartz, epidote, magnetite, albite and 271 K-feldspar (Fig. 5d-e). Amphibole, prehnite and guartz represent ~ 60-70 vol.% of the 272 vein and they occur as euhedral to subhedral crystals (up to ~ 4 mm in size). Epidote is 273 abundant and crystallized as subhedral to euhedral crystals (< 1 mm in size). Albite, K-274 feldspar, and magnetite are also observed as medium to fine grains. 275

The apatite ores crosscut medium- to coarse-grained country mesocratic to melanocratic pale magmatic rocks with a primary paragenesis associating albitic plagioclase (60–65 vol.%) and amphibole (20–35 vol.%) (Fig. 5f). Clinopyroxene is also present and is frequently associated with Fe-Ti oxides (magnetite and ilmenite). Quartz and K-feldspar are rare. Titanite, rutile, and apatite are the main observed accessory minerals, and epidote, chlorite, and prehnite occur as secondary phases.

282 4.5. Tasraft

Two types of apatite occur at Tasraft: (i) the first one is similar to the apatites found in Ait Daoud-Toumliline (up to 2 cm in size, dark green translucent crystals with moderate vitreous luster and often containing tiny needle-shaped amphibole inclusions,

Fig. 6a); (ii) the second one corresponds to fine crystals (less than 0.5 cm in size) of 286 gem-quality apatite with a color, transparency and luster similar to those found in 287 Tirrhist-Inouzane and Anemzi. The gangue of these fine apatite gems consists mainly of 288 clinopyroxene, albite, quartz, K-feldspar, and titanite (Figs. 6b, c, d, e). As observed for 289 Tirrhist-Inouzane, clinopyroxene (up to 45 vol.% of the vein) is often zoned and occurs 290 291 as euhedral to subhedral crystals (up to 1 cm in size). Albite (dominant), K-feldspar, and guartz represent around 40 vol.% and occur as medium euhedral to anhedral crystals (~ 292 0.1–1 mm in size), interstitial between clinopyroxene and apatite. Titanite is present and 293 occurs as green-yellowish to clear prismatic crystals (< 5 vol.%, up to 1 cm in size). 294

The host rocks of these apatite veins are coarse- to medium-grained leucocratic magmatic rocks containing up to 70–80 vol.% of albitic plagioclase, up to 10 vol.% of clinopyroxene and subordinate K-feldspar and quartz. Amphibole, magnetite, titanite, rutile, apatite and zircon are accessory minerals (Figs. 6b–c). Epidote, chlorite, and sericite also occur as secondary phases.

300 5. Geochemistry of magmatic host rocks

Whole-rock geochemical analyses for the magmatic facies directly hosting the Moroccan Central High-Atlas vein-type apatite ores are given in Table 2. In the TAS classification (Fig. 7a; Middlemost, 1994), these rocks have intermediate to felsic (dominant) signature with SiO₂ contents ranging from ~ 53 to 65 wt.% and plot in the fields for gabbrodiorite–monzodiorite and syenite–quartz monzonite (dominant). They belong mostly to the alkaline/sub-alkaline series with alkali (K₂O + Na₂O) content from ~ 4.6 to ~ 10 wt.%. All these facies have relatively large ranges in Fe₂O₃^{tot} (~ 2–10.3

wt.%), MgO (Mg# ~ 0.04–0.8), CaO (~ 1.7–10.6 wt.%), Al₂O₃ (14.2–16.5 wt.%), TiO₂ (~ 308 0.4-2.3 wt.%) and P₂O₅ (~ 0.03-0.9 wt.%). Almost all these rocks are peralkaline [mol. 309 $(Al_2O_3/CaO + Na_2O + K_2O) = ACNK = 0.51-0.94$ with low K contents [K# = mol. 310 $(K_2O/Na_2O+K_2O) = 0.01-0.1$, except for Anemzi samples that belong to the high-K 311 serie (K#: 0.26- 0.36) (Fig. 7b, Table 2, e.g., Rickwood, 1989; Maniar and Piccoli, 312 313 1989). Compared to the available data from the literature for the same Central High-Atlas magmatic intrusions further away from the apatite veins (Figs. 7a-c; data from 314 Armando, 1999; Lhachmi et al., 2001; Zayane et al., 2002; Essaifi and Zayane, 2018), 315 the studied rocks have geochemical compositions similar to the more differentiated 316 members and differ significantly from the more primitive members (mostly gabbros). 317 Evaluation of the alteration effects using the discriminated diagram of Hughes (1973) 318 shows that almost all these differentiated rocks plot toward the field of sodic series 319 $(Na_2O up to \sim 9 wt.\%)$, suggesting that they might have been affected by general Na-320 metasomatism conditions (Fig. 7c). In terms of volatile element compositions, CI and 321 SO₃ content reaches, respectively, a maximum of 0.25 wt.% and 0.04 wt.% in the Ait 322 Daoud-Toumliline samples and are lowest in the other samples (0.05-0.13 wt.% Cl and 323 0.01 wt.% SO₃) (Table 2). Besides, all investigated rock samples have moderate 324 contents of MnO (0.03–0.12 wt.%), Co (53–155 ppm), Ni (29–133 ppm), Cu (17–55 325 ppm), Zn (14-50 ppm), Ga (18-47 ppm), Sr (213-407 ppm), and Y (15-103 ppm). 326 327 However, the more felsic rocks have slightly high Zr (up to 748 ppm) and Nb (up to 120 ppm) concentrations, and low values of Cr (less than 32 ppm) (Table 2). 328

329 6. Mineralogy

330 6.1. Apatite

331 6.1.1. Major element composition

Table 3 shows representative major element analyses of the studied apatites. 332 The two major constituents —i.e., CaO and P_2O_5 — show rather little variations: CaO 333 and P₂O₅ vary between 53 and 57 wt.% and between 39 and 44 wt.%, respectively. The 334 335 F content of the Anemzi apatite associated with calcite, feldspars, and magnetite matrix (white gangue; see above) is quite homogenous with about 2 wt.% and low CI content 336 (0.67-0.90 wt.%). In contrast, the Anemzi apatites associated with dark gangue 337 (amphibole matrix), are rather heterogeneous: their F contents decrease from core to 338 rim (from ~ 1.9 to ~ 0.8 wt.%) while Cl increases (from ~ 0.6 to ~ 2.5 wt.%) (Table 3). All 339 analyzed Tirrhist-Inouzane apatites have relatively homogeneous F and CI contents (~ 340 1.9-2.4 and ~ 0.34-0.47 wt.%, respectively). Similarly, the apatites from Tassent and 341 Tasraft (fine gems) have F concentrations between 1.7 and 2.8 wt.% and low to 342 moderate CI contents (0.5–1.47 wt.%). On the other hand, distinct apatite compositions 343 have been yielded by amphibole-bearing apatites from both Tasraft and Ait Daoud-344 Toumliline: the first ones show compositions intermediate between those of Cl-rich 345 apatites and those of CI-F apatites (F contents vary between 0.47 and 1.47 wt.% and CI 346 between 3.44 and 1.5 wt.%); the second ones are CI-rich apatites with high CI (up to 3.3 347 wt.%) and low F (~ 0.6–1 wt.%) contents. If we considered all apatites analyses, they 348 349 show a good linear trend and progressive compositional variations from the F-rich to Clrich apatites as shown by Fig 8a. 350

In all studied apatites, the element substitutions are always very low, and they 351 vary between the different apatite deposits and even between the crystals of the same 352 deposit (see Table 3 and Figs. 8b, c, d). The major substituent element is Si (0.1 < SiO₂) 353 wt.% < 0.8). Na₂O contents can reach 0.55 wt.%, whereas FeO^{tot} and MgO never 354 exceed 0.11 and 0.08 wt.%, respectively. The S contents are particularly variable: SO₂ 355 varies between 0 and 0.57 wt.%. In detail, the amphibole-bearing apatites from Ait 356 Daoud-Toumiline and Tasraft show guite similar compositions with relatively high Na₂O 357 and MgO contents (up to 0.57 wt.% and 0.9 wt.%, respectively), FeOtot contents 358 between 0.04 and 0.11 wt.% and low concentrations of SiO₂ (< 0.4 wt.%) and SO₂ (~ 0-359 0.3 wt.%). Similar FeO^{tot} and SiO₂ abundances (0.04–0.10 wt.% and 0.18–0.40 wt.%, 360 respectively) have been measured in Tassent apatite but with generally low Na₂O 361 (0.06–0.29 wt.%) and SO₂ (< 0.04 wt.%) contents and no MgO. The apatites from 362 Tirrhist-Inouzane and Tasraft (fine gems) have MgO below detection limit and they 363 generally contain similar low Na₂O (\leq 0.08 wt.%) and FeO^{tot} (\leq 0.04 wt.%) 364 concentrations, whereas SiO₂ (up to 0.76 wt.%) and SO₂ (0.30–0.57 wt.%) abundances 365 are relatively high. The Anemzi apatites from both white and dark gangues have 366 comparable Na₂O (0–0.15 wt.%), MgO (\leq 0.01 wt.%) and FeO ^{tot} (0.02–0.09 wt.%) 367 concentrations. However, these two types of apatite are distinguished by their SiO₂ and 368 SO₂ contents: the apatites from the dark gangue have SiO₂ (0.12–0.32 wt.%) and SO₂ 369 370 (0–0.04 wt.%) significantly lower than those of the white gangue apatites (0.62–0.70 and 0.01–0.42 wt.%, respectively). 371

In addition, the rim–core chemical variations (e.g., SiO_2 , FeO^{tot} , Na_2O , CI, and F) in some apatite crystals of veins are shown in Figs. 8e–h and Table 3. Despite their

large size, almost all fluorapatites —e.g., Tirrhist-Inouzane and Anemzi (white gangue)— have no chemical zoning. In contrast, the Anemzi amphibole-bearing apatites (dark gangue) display F-rich cores and Cl-rich rims and the SO₂ contents decrease from core to rim while Na₂O contents increase (Table 3).

To further constrain the relationships between the apatites and their magmatic 378 host rocks, the apatites in Tirrhist-Inouzane syenites have also been analyzed (see 379 Table 3). These igneous apatite grains have similar compositions compared to the 380 Tirrhist-Inouzane, Anemzi (white gangue), Tassent and Tasraft (fine gems) apatite 381 crystals in veins in terms of F (2–2.3 wt.%), Cl (0.5–0.8 wt.%), Na₂O (0.1–0.19 wt.%), 382 MgO (< 0.01) and FeO^{tot} (0.04–0.09 wt.%), and they are clearly distinguished from both 383 384 Ait Daoud-Toumliline and Tasraft amphibole-bearing apatite gems in veins as shown by Figs. 8a–c and Table 3. On the other hand, SiO_2 and SO_2 abundances in the syenite 385 386 apatites are similar to those found in the gemmy apatites in veins from Tassent and 387 Anemzi (dark gangue) (SO₂ <0.04 wt.%, SiO₂ ~ 0.35 wt.%) (Fig. 8d).

388 6.1.2. Trace element composition

The trace element abundances of studied apatites given in Table 3 show that these minerals can incorporate a wide range of trace elements and often in large quantities. The most abundant trace elements in the Central High-Atlas gem-quality apatites in veins are REE (mainly La, Ce and Nd), Sr, Y, V, Mn, Th and U, whereas Sc, Co, Rb, Zr, Nb, Ba and Pb contents are very low (< 6 ppm) (Fig. 9 and Table 3). The highest REE concentrations are observed in the Ait Daoud-Toumliline apatites (ΣREE: 18190–22587 ppm), with variable abundances in the Anemzi (white gangue) and

Tasraft amphibole-bearing apatites (ΣREE : 3846–17432 ppm), moderate contents in 396 Tassent apatites (ΣREE : 13140–13554 ppm) and low to moderate values (ΣREE : 397 4823–8495 ppm) in Tirrhist-Inouzane, Anemzi (dark gangue) and Tasraft (fine gems) 398 apatites. Figs. 10 and 11 show, respectively, their REE patterns and multi-element 399 spider diagrams normalized to chondrite abundances from McDonough and Sun (1995). 400 In all apatites, a pronounced negative Eu-anomaly can be observed (0.11 < Eu/Eu* < 401 0.63; Fig. 10). Almost all analyses show consistent enrichment in light REE relative to 402 heavy REE with $(Ce/Yb)_n$ ratios ranging from 12 to 78. 403

The V contents of apatites vary greatly between the different deposits. They are 404 very low (between 3 and 4 ppm) in the Tassent apatites and slightly higher (between 18 405 and 34 ppm) in the Tirrhist-Inouzane and high in Ait Daoud-Toumliline (55-77 ppm) 406 (Fig. 9a). We also find these high values but with variability in both Tasraft apatite types: 407 3–128 ppm in the amphibole-bearing apatites and 96–146 ppm in the fine apatite gems. 408 409 In Anemzi, the V contents of the apatites from the dark gangue are low but relatively constant (9–14 ppm), while these from the white gangue are surprisingly variable and 410 411 they can even reach high values (0.17–128 ppm) as in Tasraft. The Mn contents are 412 very variable in the Anemzi apatites from the white gangue (56–397 ppm), while they are relatively stable in those from the dark gangue (274-312 ppm) (Fig. 9b). These 413 latter values are relatively close to that found in the Tassent apatites (222-241 ppm) 414 Mn). The two types of apatite from Tasraft have Mn contents significantly different: 63-415 96 ppm for the fine gem-crystals and 138-250 ppm for the Amp-bearing crystals. The 416 Mn contents of the apatites from Tirrhist-Inouzane (140-148 ppm) and Ait Daoud-417 Toumliline (116–131 homogeneous and quite similar. Strontium ppm) are 418

concentrations are moderate to high in all studied apatites (Fig. 9c): 407-686 ppm in 419 Anemzi white gangue, 673–792 ppm in Anemzi dark gangue, 763–781 ppm in Tirrhist-420 Inouzane, 720–730 ppm in Tassent, 382–764 ppm in Tasraft and 386–483 ppm in Ait 421 Daoud-Toumliline. Yttrium concentration ranges from 230 ppm to 4118 ppm (Fig. 9e): 422 1567–1672 ppm in Tassent, 1454–1692 ppm in Ait Daoud-Toumliline, 230–4118 ppm in 423 Anemzi (white gangue), 425–947 ppm in Anemzi (dark gangue), 358–696 ppm in 424 Tirrhist-Inouzane and 240–979 ppm in Tasraft. Thorium concentrations are moderate to 425 high and usually ranges from 76 ppm to 530 ppm (Fig. 9f): 90-227 ppm in Anemzi white 426 427 gangue, 79–112 ppm in Anemzi dark gangue, 140–182 ppm in Tirrhist-Inouzane, 76–83 ppm in Tassent, 63–253 ppm in Tasraft and 183–253 ppm in Ait Daoud-Toumliline. 428 Uranium concentrations vary generally from 1.5 to 26 ppm (Fig. 9g). Rather similar high 429 U values (16–26 ppm) are found in the apatites form the Anemzi (white gangue), 430 Tirrhist-Inouzane and Tasraft (fine gems). The lowest U contents (1.5–7 ppm) are found 431 in Tassent and mostly in amphibole-bearing apatites from Anemzi (dark gangue) and in 432 these from Ait Daoud-Toumliline and Tasraft. 433

In addition, if we considered all apatites analyses from all studied veins, they show a rough positive correlation between total REE and Na₂O from the less to more Cl-rich apatites as shown by Fig 12. Although some compositional variations can be observed among the different apatites in veins (Figs. 9, 10, 11, 12, Table 3), their REE and multi-trace element patterns overlap and are globally parallel with those of the magmatic host rock apatites investigated here (Figs. 10–11).

440 6.2. The gangue minerals

441 6.2.1. Clinopyroxene

Clinopyroxene is exclusively observed in the F-rich apatites veins (e.g., Figs. 3, 4 442 and 6). The crystals are euhedral, up to 3 cm in size and dark to light green in color, 443 sometimes with well-marked zoning corresponding to an alternation of dark and light 444 green domains. Dark and light green grains also occur in almost all magmatic rocks 445 hosting the apatite veins: they appear as euhedral to subhedral grains (0.5 and 2 mm, 446 Figs. 3–4, 6). Major and trace element abundances of clinopyroxenes are given in 447 Tables 4–5. The two major constituents -i.e., SiO₂ and CaO- show little variations; 448 the representative values are ~ 49-54 wt.% SiO₂ and 20-26 wt.% CaO. In detail, all 449 analyzed dark green clinopyroxene zones and crystals from both apatite-bearing veins 450 and country alkaline rocks are similar and have hedenbergite to Fe-rich augite 451 452 compositions (Wo₄₄₋₄₉, En₁₂₋₂₆, Fs₂₇₋₄₃, see Fig. 13a and Table 4; e.g., Morimoto et al., 1988) with low Mg# [Mg/(Mg + Fe²⁺) ~ 0.32–0.66], high total FeO content (~ 16–23 wt. 453 %), and moderate to high Na₂O values (up to \sim 3 wt. %) and MnO (up to 1.4 wt. %). 454 455 However, the light green zones and crystals, are mainly diopside in compositions (Wo₄₆₋ $_{51}$, En₂₇₋₄₁, Fs₈₋₂₅) with high Mg# ~ (up to 0.95), and low total FeO content (~ 5–14 wt. 456 %), MnO (~ 0.1–0.4 wt. %) and Na₂O values (mostly < 2 wt. %). All these clinopyroxene 457 types have similar variable compositional range, with, Al₂O₃ (~ 0.1–2.6 wt. %), TiO₂ 458 459 (mostly < 1 wt. %) and Cr_2O_3 (0–0.07 wt. %) contents.

460 Fig. 13b shows REE patterns normalized to chondrite values (McDonough and 461 Sun, 1995) of clinopyroxenes from Tasraft and Tassent F-rich apatite veins, and

462	Tirrhist-Inouzane host syenites (Table 5). All clinopyroxene REE concentrations are 10-
463	160 times enriched relative to chondrite abundances ($\Sigma REE \sim 80-147$ ppm). They have
464	parallel REE patterns [with slight high values in light REE in clinopyroxene from Tasraft
465	apatite veins with (La_n/Yb_n) up to 1.3] and show strongly developed negative Eu
466	anomaly (Eu/Eu* ~ 0.19–0.37). General high depletion for Cu, Rb, Ba, Nb, Ta, Pb, Th,
467	and U (< 0.07 ppm) is present for all analyzed clinopyroxenes. They have generally \sim
468	3–12 ppm Sc, 9–23 ppm Co, ~ 17–80 ppm Sr, ~ 26–98 ppm Zn, and ~ 23–166 ppm V.

469 6.2.2. Amphibole

Amphibole occurs as main gangue mineral in CI-rich apatites veins (e.g., Ait-470 Daoud-Toumliline; Fig. 5) and as inclusions in almost all the Cl-rich apatites (e.g., Ait 471 Daoud-Toumliline, Tasraft and Anemzi; Figs. 2, 5-6). It forms euhedral and acicular 472 green to brown crystals up to 2 cm in size. Amphibole also occurs as euhedral to 473 474 subhedral grains (~ 0.2–1 mm in size) in magmatic host rocks with colors similar to that of amphibole from apatite veins (e.g., Figs. 4–5). Table 4 shows representative major 475 element compositions of the amphiboles. All amphiboles from apatite veins and their 476 477 host rocks are calcic with high Ca content (~ 1.67-2.10 atoms per formula unit = a.p.f.u), Si (~ 6.87-7.78 a.p.f.u) and Mg (Mg# ~ 0.60 to 0.90) with moderate Fe (mostly 478 ~ 0.54-1.20 a.p.f.u), low to moderate (Na+K) values (0.18-0.90 a.p.f.u) and low Al 479 480 concentrations (~ 0.1-1 a.p.f.u), characteristics of magnesiohornblende-actinolite and edinite association (Fig. 13c; e.g., Leake et al., 1997). The amphibole trace element 481 abundances have been analyzed for Anemzi apatite veins (dark gangue) and are given 482 483 in Table 5. The REE abundance in amphiboles range from 46 to 101 ppm. In general,

their chondrite-normalized REE patterns are remarkably constant (Fig. 13d): they all display a gentle shape, flat pattern ($La_n/Yb_n \sim 0.7-1$) with a pronounced negative Eu anomaly (Eu/Eu* ~ 0.4–0.5) similar to those of clinopyroxenes (Fig. 13c). They also have 32–650 ppm Cr and 364–405 ppm V, and Sc, Co, Zn, Sr, Y, Zr, and Nb abundances are less than 68 ppm, with low values (< 2 ppm) for Cu, Rb, Ba, Ta, Pb, Th, and U (Table 5).

490 6.2.3. Feldspars

Feldspars are commonly present in all studied vein-type apatite ores. Table 6 491 displays representative feldspar analyses. In all apatite ores and magmatic host rocks 492 (Figs. 2–6), albite is the most abundant feldspar: the crystals are euhedral to subhedral 493 and of centimeter size (up to 5 cm). Their compositions are similar, and they correspond 494 almost pure to albite (Ab ~ 90 to 100). K-feldspar is also present but less abundant than 495 496 albite: the crystals are euhedral to subhedral in the veins, subhedral to anhedral in magmatic host rocks and with sizes varying between 0.1 and 1 cm. Their compositions 497 are between Or_{94} and Or_{99} . Anorthoclase compositions (Ab ~ 70–75, An ~ 1–3, Or ~ 498 499 23–29) are exclusively found in the magmatic host rocks (see Table 6).

500 6.2.4. Other minerals

501 Magnetite is found in all apatite veins: the crystals are euhedral to subhedral with 502 up to 1 cm in size. This oxide is also observed in magmatic host rock as subhedral to 503 anhedral grains up to 2 mm in size (e.g., Fig. 3). Representative compositions are 504 reported in Table 7. Analyses of magnetite indicate moderate to high FeO^{tot} contents of

about ~ 91–95 wt.% in the apatite veins. In the magmatic host rock, the magnetite composition varies from magnetite (FeO^{tot} ~ 90–95 wt.%) to Ti-magnetite [FeO^{tot} ~ 87 wt.% and TiO₂ ~ 3 wt.%], sometimes with ilmenite exsolutions (TiO₂ ~ 45–54 wt.% and FeO^{tot} ~ 46–50 wt.%) (Table 7).

Titanite is also present in both apatite veins and host rocks and the analyses are 509 reported in Table 7. It is associated with apatite veins and forms greenish yellow 510 euhedral crystals up to 2 cm in size; in magmatic host rocks, it occurs as dark brown to 511 colorless euhedral to subhedral crystals (0.5–2 mm). Titanite from veins has relatively 512 homogeneous contents in SiO₂. TiO₂, and CaO (~ 29.5, ~ 41.5 and 29 wt.%) 513 respectively), whereas in the host rocks the titanite compositions are more variable: 20-514 515 32 wt.% SiO₂, 29–54 wt.% TiO₂ and 19–29 wt.% CaO. On the other hand, rutile is observed and analyzed exclusively in the magmatic host rock, forming small euhedral to 516 suhedral dark-red grains (up to 0.2 mm in size) and its analyses are also given in Table 517 518 7.

In the apatite mineralized veins, epidote (pistachite) occurs as green to greenish yellow euhedral crystals up to 3 cm in size, whereas in the alkaline host rocks it appears as yellow subhedral to anhedral grains of small size (0.02-0.5 cm). As shown in Table 8, the epidote compositions are similar in veins and their host rocks: 36-38 SiO₂ wt.%, 18.50-22.70 Al₂O₃ wt.%, 21-25 CaO wt% wt.%, with slight variation FeO^{tot} content (~ 10-18 wt.%).

525 Prehnite is observed in the Tassent and Ait Daoud-Toumliline apatite mineralized 526 veins. It occurs as radiating fibrous aggregates and is commonly translucent with

colorless to white greenish color (up to 4 cm in size, e.g., Figs. 4–5). Prehnite can occur
also in the magmatic host rocks where it appears both as veinlets and as microcavity
filling products. Analyses of this calcic mineral (~ 28 wt.% CaO) are shown in Table 8
and are homogenous and similar in both mineralized veins and host alkaline rocks.

531 **7. Discussion and conclusions**

According to our field observations, and petrological, mineralogical, and 532 geochemical study, all Moroccan Central High-Atlas vein-type apatite ores (mostly gem-533 534 quality) are hosted by differentiated igneous intrusions ranging from syenite-quartz monzonite (dominant) to monzodiorite-gabbrodiorite (Fig. 7 and Table 2). The spatial 535 association with Mesozoic (Jurassic-Cretaceous) alkaline/transitional rocks is typical of 536 phosphates derived from silicate alkaline-carbonatite complexes (e.g., Simandl and 537 Paradis, 2018 and references therein). However, carbonatites have not been found in 538 the studied area, although the ore bodies are not so far to the well-known Tamazeght 539 Eocene carbonatite complex (see Fig. 1b). 540

Our new data lead us to distinguish two types of apatite ores: (i) high gem-guality F-rich 541 apatites associated with clinopyroxene (diopside to hedenbergite-augite) and (ii) gemmy 542 Cl-rich apatites mainly formed in an amphibole matrix (hornblende-edenite to actinolite) 543 (Figs. 2–6, 8, Table 3). Both ore bodies are also associated with feldspars (albitic 544 plagioclase dominant and orthoclase), guartz, magnetite, titanite, epidote, calcite, and 545 prehnite. All studied apatites of both deposit types have similar REE and multi-trace 546 element patterns which suggest that they could have a relatively close origin (Figs. 9, 547 10, 11, Table 3). A comparison between the Central High-Atlas apatites and those of 548

the well-known Sweden Kiruna-type iron ores which formed by late-stage of magmatic 549 differentiation of felsic magmas (pink field in Fig. 10; data from Frietsch and Perdahl, 550 1995) shows that the REE compositions of apatites from both deposits are similar with 551 pronounced negative Eu anomaly. Conversely, they differ from the REE patterns of the 552 worldwide carbonatite apatites from the Oka (Canada), Kaiserstuhl (Germany), 553 Jacupiranga (Brazil), Fen (Norway), Sokli (Finland), Hörningsholmen-Alnö (Sweden), 554 Siilinjärvi (Finnland) and Loolekop-Phalaborwa (South Africa) complexes (green field in 555 Fig. 10; data from Ingrid, 1998; Chen and Simonetti, 2013; Doroshkevich et al., 2018; 556 557 Decrée et al., 2020) (Eu/Eu* up to 0.63 in our apatites and around 1 in worldwide carbonatite apatites). The pronounced Eu negative anomaly exhibited by all the Central 558 High-Atlas apatites studied strongly suggests that feldspar crystallized from phosphate-559 rich melt prior to apatite crystallization. Such negative Eu anomalies in apatite have also 560 been reported in fenites (Eu/Eu* ~ 0.73–0.84, e.g., Decrée et al., 2020) as a result of 561 cooling and crystallization of carbonatitic and alkaline magmas in the crust and the 562 presence of alkali-rich fluids that metasomatize the surrounding country rocks (e.g., 563 Elliott et al., 2018 and references therein). Although many of the mineralogical features 564 565 observed in studied apatite veins (evidence of e.g., K-feldspar, albite, clinopyroxenes and calcic amphiboles and other accessory minerals, Figs. 2–6) and the extensive sodic 566 metasomatism affecting the magmatic country rocks (Fig. 7) suggest that fenitization 567 568 may have occurred during the crystallization of apatite-rich veins (e.g., Zharikov et al., 2007; Elliott et al., 2018). The pronounced Eu anomaly together with Sr, Y, and Mn 569 570 contents (Fig. 14a-b; Belousova et al., 2002) strongly indicate that Central High-Atlas 571 apatites are co-genetic and chemically similar to the magmatic apatites of granitoids of

Kiruna type iron ores (Fig. 14a-b). Indeed, the mineralogical and geochemical signature 572 of the Central High-Atlas apatite vein-type ores may be related to host-alkaline magma 573 crystallization and evolution rather than carbonatite magma. These observations are 574 corroborated by apatite discrimination diagrams based on the concentrations of several 575 trace elements in apatite (Figs. 14c-d; Mao et al. 2016), showing that the Central High-576 577 Atlas apatites have composition close to apatites from iron oxide copper gold (IOCG) ore deposits and unmineralized rocks (likely syenites) (Fig. 14c). Generally, the IOCG 578 systems are clearly interpreted as origin from magmatic hydrothermal systems (mainly 579 580 porphyries, e.g., Barton, 2009). In addition, the mineralogy, texture, alteration halos and geochemistry data also suggest that the Central High-Atlas vein-type apatite ores could 581 be largely linked to the Central High-Atlas differentiated magmatic rocks (mostly 582 syenites) (Figs. 9, 10, 11, 12, 14). Plagioclases in both veins and host-rocks indicate 583 that both derived from sodic-rich melt or/and underwent general albitization (see above 584 and Table 6, Fig. 7b-c). The clinopyroxene and amphibole observed in both units (veins 585 and host rocks) refer both to Ca-rich minerals and support a common igneous origin 586 (Table 4-5 and Fig. 13). Altogether, field observations and mineralogical and 587 588 geochemical signatures of veins and host-rocks suggest that Moroccan Central High-Atlas apatite ores might be related to the magmatic processes that lead to the formation 589 590 of differentiated rock (likely syenites), although hydrothermal/continental contamination 591 may have also been involved.

The absolute age of these apatite deposits is elusive, but they are observed in veins crosscutting the Jurassic-Cretaceous (ca. 165–125 Ma) alkaline igneous rocks of the Central High-Atlas and are probably coeval or post-date the crystallization of the

magmatic intrusions. The geochemical observations suggest that the crystallization 595 environment of the high quality F-rich apatite ores (e.g., Figs. 2–3) remained chemically 596 stable and that the intensive parameters controlling their crystallization process did not 597 fluctuate (Fig. 8, Table 3). In contrast, the CI-rich apatite ores enclosing intense 598 randomly distributed amphibole inclusions in apatite gems indicate slight fluctuation of 599 600 magma and/or fluid compositions. The presence of low temperature minerals (albite, guartz, epidote, prehnite, K-feldspar, magnetite and calcite) in both apatite deposits and 601 in their host alkaline rocks strongly suggest that crystallization occurred during late 602 603 magmatic stages and that the main geochemical signatures of apatite are most probably related to crystallization of alkaline magma rich in P and incompatible 604 elements such as F (e.g., Fig. 8). It is also important to note that interactions of evolved 605 magma with country sedimentary formations rich in Cl, Na and Ca most probably 606 participated to the CI-Na enrichment of apatites cannot be ignored. In Fig. 15, we 607 provide the suitable fluids involved during the formation of the Central High-Atlas apatite 608 mineralization. In the igneous systems the apatite is initially enriched in F owing to the 609 high apatite-melt partition coefficient for F relative to CI (e.g., Harlov, 2015; Webster 610 611 and Piccoli, 2015). Throughout progressive crystallization of the magmas, the F contents decrease due to the crystallization of F-rich apatite resulting in progressive CI 612 enrichment of apatite (e.g., Fig. 8a and Table 3), Anemzi amphibole-bearing apatites 613 614 being an intermediate case between the purely F-rich (e.g., Anemzi white gangue, Tirrhist-Inouzane, and Tassent) and Cl-rich apatite deposits (e.g., Tasraft and Ait 615 Daoud-Toumliline). As mentioned above, the genesis of the Cl-rich apatites could also 616 result from contamination of magma by CI-enriched hydrothermal fluids due to 617

percolation through Triassic evaporates (mainly halite) buried beneath the Moroccan 618 Central High-Atlas belt (Fig. 1c). This might be related to halokinetic tectonic on the 619 Central High-Atlas magmatic intrusions emplacement (e.g., Michard et al., 2011; Saura 620 et al., 2014) and a general Na-metasomatism/fenitization associated with the 621 emplacement of the alkaline magmatic rocks directly hosting these vein-type apatite 622 623 ores (see Fig. 7; e.g., Zirner et al., 2015; Essaifi and Zayane, 2018). The presence of solid and fluid organic inclusions in Anemzi gemmy apatites (Dumańska-Słowik et al., 624 2018), also supports a contamination of magmas by country sedimentary rocks. In 625 addition, the hydrothermal fluids could also percolate through Mg-rich rocks (likely 626 gabbros) present in the same area as attested by the presence of MgO in Cl-apatites 627 (e.g., Fig. 8, Table 3). Altogether, this study highlighted the role of magma/rock and 628 fluid/rock interactions and the complex chemical reactions involved during magma 629 emplacement and the genesis of phosphate ores deposits. Further detailed field, 630 petrological, structural, geochemical, geochronological and isotope investigations are 631 however necessary in order to better quantified the igneous and sub-solidus processes 632 as well as the exchange reactions and environmental conditions that lead to igneous 633 634 phosphate ores deposits and the crystallization of gem-quality apatite crystals.

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922 Figure captions

- **Fig. 1. (a)** Sketch map showing the location of Central High-Atlas (CHA) segment in the
- north Morocco. (b) Geological map and (c) NW-SE cross-section of the Central High-
- 925 Atlas [adapted from Teixell et al. (2003), Michard et al. (2011) and references therein],
- showing the spatial relationships among the Jurassic-Cretaceous alkaline magmatism
- and the Mesozoic sedimentary series, and location of the studied apatite deposits.
- Fig. 2. (a–b) Hand specimen and (c–e) microscopic photographs of the Anemzi apatite
 ores showing gangue- and host rock-forming minerals: (a, c, d) white and (b, e) dark
 gangue types. Apatite (Ap), plagioclase (PI), K-feldspar (Kfs), calcite (Cal), magnetite
 (Mag), quartz (Qz), amphibole (Amp).
- Fig. 3. (a, b) Hand specimen and (c, e, f, d) microscopic photographs of the TirrhistInouzane apatite mineralization showing gangue- and host rock-forming minerals.
 Clinopyroxene (Cpx), epidote (Ep), stilpnomelane (Stp).
- **Fig. 4. (a, b)** Hand specimen and **(c, d, e)** microscopic photographs of the Tassent apatite mineralization showing gangue- and host rock-forming minerals. Prehnite (Prh), titanite (Ttn).
- **Fig. 5. (a, b, c)** Hand specimen and **(d, e, f)** microscopic photographs of the Ait Daoud-Toumliline apatite mineralization showing gangue- and host rock-forming minerals.

Fig. 6. (a) Amphibole-bearing apatite gem in mount, (b) hand specimen and (c, d, e)
microscopic photographs of the Tasraft apatite mineralization (fine gems), showing
gangue- and host rock-forming minerals.

Fig. 7. Chemical classification for the lithologies hosting the Central High-Atlas veintype apatite deposits. **(a)** TAS classification diagram (Middlemost, 1994). **(b)** K_2O vs. SiO₂ diagram of Rickwood (1989). **(c)** (K_2O +Na₂O) vs. [$K_2O/(K_2O+Na_2O)$]*100 plot (after Hughes, 1973). Literature data compiled from Armando (1999), Lhachmi et al. (2001), Zayane et al. (2002) and Essaifi and Zayane (2018).

Fig. 8. (a–d) Major element concentrations in Central High-Atlas apatites. (e–h) Results
of electron microprobe analytical profiles, and trends within images of apatite crystals
corresponding to locations of these profiles.

Fig. 9. Compositional variation diagrams for the most abundant trace elements inCentral High-Atlas apatites.

Fig. 10. REE patterns normalized to chondrites (McDonough and Sun, 1995) for the
Central High-Atlas apatites. Worldwide carbonatite apatite data are from Ingrid (1998),
Chen and Simonetti (2013), Doroshkevich et al. (2018) and Decrée et al. (2020). Iron
ore apatite data are from Frietsch and Perdahl (1995).

Fig. 11. Spider diagrams normalized to chondrites (McDonough and Sun, 1995) for the
Central High-Atlas apatites.

Fig. 12. Σ REE (ppm) versus Na₂O content (wt.%) in apatite from veins and host rocks.

Fig. 13. Classification and REE patterns normalized to chondrites (McDonough and
 Sun, 1995) of studied clinopyroxenes and amphiboles: (a, b) clinopyroxenes and (c, d)
 amphiboles.

Fig. 14. (a-b) Trace element discrimination diagrams for studied Central High-Atlas 963 apatites, compared to those of reference rock types (Belousova et al., 2002). 964 Carbonatite field from Ingrid (1998), Chen and Simonetti (2013), Doroshkevich et al. 965 (2018) and Decrée et al. (2020). Field of carbonatite related fenite apatites is plotted 966 using data from Decrée et al. (2020). (c-d) Apatite metallogenic discrimination diagrams 967 of Mao et al. (2016). DP1-1 [= -0.06461logMn - 1.56logSr + 2.609logY + 0.3631logLa -968 1.766logCe + 0.6243logEu - 3.642logDy + 0.7086logYb - 1.178logPb + 0.4161logTh + 969 970 0.963logU + 6.589]. DP1-2 [= 0.2073logMn - 1.035logSr + 15.1logY + 4.995logLa -5.804logCe + 0.1741logEu - 8.771logDy - 4.326logYb + 2.022logPb - 0.6719logTh + 971 0.02096logU - 10.45]. DP4-1 [= 5.379·logV + 1.0285·logMn + 1.0004·logSr -972 0.0447·logCe + 3.169·logEu - 5.412·logYb - 0.3302·logPb - 0.1080·logTh + 5.385]. 973

Fig. 15. A schematic model for the two main Central High-Atlas vein-type apatite ores.

976 **Tables**

977 **Table 1.** Selected samples of the studied apatite deposits for mineralogical and978 geochemical analysis.

Table 2. Whole-rock XRF analyses of alkaline rocks directly hosting the Central HighAtlas vein-type apatite ores.

Table 3. Representative major and trace element compositions of the studied CentralHigh-Atlas apatites.

Table 4. Representative compositions (wt.%) of the clinopyroxenes and amphiboles in

the Moroccan Central High-Atlas apatite mineralized veins and magmatic host rocks.

985 **Table 5.** Trace element compositions (ppm) of the studied clinopyroxenes and 986 amphiboles.

Table 6. Representative compositions (wt.%) of the feldspars in the studied CentralHigh-Atlas apatite ores and their host alkaline rocks.

Table 7. Representative compositions (wt.%) of the magnetite, ilmenite, titanite andrutile from studied apatite veins and their host alkaline rocks.

Table 8. Representative compositions (wt.%) of the epidote and prehnite associated theapatite ores and their host alkaline rocks.