

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

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- 1 Petrological and geochemical constraints on the origin of apatite
- 2 ores from Mesozoic alkaline intrusive complexes, Central High-
- 3 Atlas, Morocco
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## 18 Abstract

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Five main apatite deposits from the Moroccan Central High-Atlas —including Anemzi, Tirrhist-Inouzane, Tassent, Ait-Daoud-Toumliline and Tasraft— have been investigated through integrated field, petrographic, mineralogical, and geochemical studies. The apatite ore occurs as veins, few mm to several cm thick, spatially associated with syenite-quartz monzonite (dominant) to monzodiorite-gabbrodiorite bodies emplaced during the Atlas Jurassic-Cretaceous alkaline magmatic event. Gemquality apatite crystals, up to 15 cm in size, are associated with albite, clinopyroxene (hedenbergite-augite-diopside), amphibole (hornblende-edenite-actinolite), K-feldspar, quartz, magnetite, titanite, epidote, prehnite, and calcite. Two types of apatite have 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 contents consistent with a magmatic origin, corroborated by the chemical similarity with accessory apatite in the host alkaline intrusions, as well as with other reference igneous apatites. However, hydrothermal fluids percolating through country sedimentary rocks were also involved, as indicated by the striking Na enrichment observed in the Cl-rich apatites, likely inherited from Triassic evaporites, showing close spatial relationships with the alkaline intrusions. These fluids would also account for pervasive Nametasomatism of alkaline magmatic rocks, as observed in the wall rocks of the apatite veins.

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

## 1. Introduction

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Apatite is the most ubiquitous accessory phosphorus(P)-bearing mineral found in 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 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, 2015; Pufahl and Groa et al., 2017). Apatite is the only major potential resource of P used in the manufacturing of e.g., nitrogen-phosphorus-potassium (NPK) fertilizers, animal feed supplements, ceramics, pharmaceuticals, textiles and batteries. The sedimentary phosphorites make the largest contribution to the world production of phosphate, whereas igneous apatite rocks account for only ~ 10 % (e.g., Jasinski, 2016; Pufahl and Groa et al., 2017). The igneous phosphate ores are nevertheless economically valuable since they provide high quality phosphate concentrates with low contents of unwanted contaminants such as Cd, As, Pb, Si and Al, and they are rich in Rare Earth Elements (REE) (e.g., Webster and Piccoli, 2015; Chakhmouradian et al 2017). In terms of world resources, Morocco is the largest holder and producer of sedimentary phosphates, with reserves estimated to represent about ~ 76 % of world reserves (e.g., Jasinski, 2016, 2019; Pufahl and Groa et al., 2017; www.ocpgroup.ma). However, Morocco also bears igneous phosphate ores, especially in the High-Atlas mountain range. Over the last two decades, gem-quality apatite crystals wellappreciated by mineral collectors and known as "Moroccan High-Atlas Imilchil-Anemzi apatite" were made available on the international mineral market (e.g., https://www.minfind.com/mineral-569173.html; https://www.mchminerals.com/finemineral-specimens/apatite-morocco; Rakovan, 2015). Despite their economic and scientific interests, only one recent study (Dumańska-Słowik et al., 2018) was devoted to the Anemzi apatite, chiefly dealing with organic inclusions, and a detailed characterization of the apatite ores remains to be done. This paper provides the first description of the main apatite deposits in the High-Atlas region. We carried out an exhaustive petrographic, mineralogical, and geochemical study (major, volatile, and trace elements) of the apatites and associated minerals, and of the host lithologies. These data are used to identify suitable sources for the phosphate mineralization.

## 2. Geological setting

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 growth started during the early Mesozoic with the reactivation of Pangea paleo-faults which delimited subsidence sedimentary basins, leading to the Atlantic Ocean opening at the NW Africa margin (e.g., Stampfli and Borel, 2002; Piqué et al., 2002; Teixell et al., 2003; Laville et al., 2004; Frizon de Lamotte et al., 2008, 2009; Domènech et al., 2015). This chain includes several segments, such as the Western, Central and Eastern High-Atlas (Fig. 1a). In contrast with the two other segments, the Central High-Atlas corresponds to the deepest part of the orogen (Fig. 1b; e.g., Teixell et al., 2003; Frizon de Lamotte et al., 2008, 2009; Gouiza et al., 2010; Michard et al., 2011). Several works have described the lithostratigraphical sequence of this belt (Fig. 1b–c; Charrière et al., 2005, 2009; Haddoumi et al., 2002, 2010; Ettaki et al., 2007; Frizon de Lamotte et al., 2008, 2009; Cavin et al., 2010; Saura et al., 2014; Charrière and Haddoumi, 2016, 2017; Cavallina et al., 2018). The first Mesozoic sediments are Triassic red argilites and

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

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In addition, the core of the Central High-Atlas anticlinal ridges is formed by an important Jurassic-Cretaceous alkaline to transitional magmatism between ~ 165 Ma and ~ 125 Ma (Fig. 1b-c; e.g., Hailwood and Mitchell 1971; Westphal et al., 1979; Beraâouz and Bonin, 1993; Rahimi et al. 1997; Armando, 1999; Haddoumi et al., 2010; Michard et al., 2011, 2013; Bensalah et al., 2013). This magmatism occurs as numerous dykes, sills and laccoliths, either intrusive along faults and narrow anticlinal ridges or intercalated in the thick Mesozoic sedimentary series (Fig. 1b-c; e.g., Armando, 1999; Teixell et al., 2003). Basaltic lava flows within wide synclines are also reported (e.g., Guezal et al., 2011; Bensalah et al., 2013; Michard et al., 2013). The magma emplacement was mainly controlled by faults coeval with halokinetic tectonic and moderate syn-schistous deformation, might link to the widespread exhumation 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., 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 rocks, which are mostly faulted (e.g., Fig. 1b-c). The tectonic boundaries are mostly vertical/sub-vertical faults marked by brecciated formation composed of fragments of igneous intrusive and carbonate rocks. However, some rare normal contacts between the intrusions and the sedimentary sequence are observed with chilled marginal magmatic rocks with carbonates recrystallization that occurred at about 300-500 °C (Lhachmi, 1992, Armando, 1999; Lhachmi et al., 2001; Essaifi and Zayane, 2018). The

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intrusive complexes include almost all terms of alkaline magma differentiation series (e.g., Armando, 1999; Lhachmi et al., 2001; Zayane et al., 2002; Essaifi and Zayane, 2018). The intrusions are made up to 60–70% of troctolites, gabbros, and monzogabbros, while the remaining volume is represented by differentiated rocks (mostly monzonites and syenites). Depside the fragmentation of the intrusive bodies 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., Armando, 1999; Lhachmi et al., 2001; Essaifi and Zayane, 2018). The evolution of the magma sequence from mafic to felsic members would be mainly linked to fractional crystallization, whereas crustal contamination during the magma ascent cannot be excluded (e.g., Armando, 1999; Lhachmi et al., 2001, Zayane et al., 2002; Essaifi and Zayane, 2018). The magmatism is interpreted to be formed in a transpressional tectonic setting where the Central High-Atlas experienced a significant uplift and orogenesis during the Jurassic (e.g., Laville and Pique, 1992), or in an asthenosphere mantle upwelling context beneath the orogen with partial melting of enriched upper mantle components without significant crustal extension (e.g., Frizon de Lamotte et al., 2009; 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-Inougzane, Tassent-Tarstaft, Tarstaft, and Ait Daoud-Toumliline deposits, Figs. 1b, c 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 the current mining is done only in an artisanal way and the only economic opportunities 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 apatite ores generated by the mineral collectors could vary between 2 and 40 m long. These apatite-producing localities are isolated and less abundant. The contacts between the apatite veins and their host magmatic rocks are mostly sharp without any clear zonation and the mineralogical compositions of the vein-type apatite ores and its host rocks from different localities are slightly variable, whereas the main components are always alkali feldspars, pyroxene, amphibole, quartz, prehnite, calcite, magnetite, epidote, and titanite (detail below).

## 3. Sampling and analytical methods

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

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 ring mill. Loss on ignition (L.O.I) was determined by drying the samples at 900°C, and ranges from 0.07 to 5.86 wt.%. (Cl, Cr, Co, Ni, Cu, Zn, Ga, Zr, Sr, Y, Nb) The analyses were performed using a sequential spectrometer Bruker AXS S4 Pioneer equipped with three analyzers (LiF200, OVO-55, PET). For X-ray fluorescence (XRF) major element, 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 precision (% RSD), measured by repeated analyses of USGS BHVO-2 and AGV-2 reference materials as external standards was better than 1.5% for all the elements except P (2.7%) (Varas-Reus et al., 2018). The other minor elements and SO<sub>3</sub> were analysed in pressed powder pellets in an independent calibration. The analyses of certified reference materials (BIR-1) have been used as external standard and the accuracies are <5% for major elements and <11% for minor elements.

In situ analyzes of major and minor elements for minerals were carried out using the Cameca SX100 Electron Microprobe at the Geosciences Montpellier (Montpellier, 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 probe current of 20 nA. The counting time was fixed at 20 s for major elements and 40 s for F, Cl, and S. Combination of natural —including fluorapatite (F, P), chlorapatite (Cl), orthoclase (K), albite (Al, Na), wollastonite (Si, Ca), forsterite (Mg, Fe), baryte (S), rhodochrosite (Mn)— and synthetic (TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>) standards are used for the calibrations. The apatite and the associated pyroxene and amphibole were analyzed for trace elements using the Laser Ablation Coupled Plasma-Mass Spectrometry (LA–ICP-

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

## 4. Petrography

## 4.1. Anemzi

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

subhedral, and small in size (< 0.5 mm). The second gangue type is dark, and it is made almost exclusively of needle-shaped amphibole (mostly hornblende) with subordinate chlorite as a product of amphibole transformation (Figs. 2b, e). The most beautiful Moroccan apatite gems are extracted from veins within white gangue: they are characterized by their perfect euhedral habit, transparency, green-yellow color and 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 needles of amphibole similar to those present in the matrix veins (Figs. 2b, e).

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 abundant (up to 20 vol.%) and it appears as subhedral to euhedral crystals (~ 0.2–1 cm in size). Albite (dominant), quartz and K-feldspar (rare) represent around 30 vol.% and occur as medium- to fine subhedral to anhedral crystals (~ 0.1–1 mm in size), filling the interstices among clinopyroxene, epidote, and apatite. These apatite veins crosscut 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 (< 5 vol.%) quartz and K-feldspar. Magnetite (sometimes with ilmenite exsolutions), stilpnomelane, apatite and zircon are also observed. Chlorite, epidote and sericite occur as secondary mineral assemblage.

#### 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.

#### 4.4. Ait Daoud-Toumliline

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

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.

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

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.

## 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  $SiO_2$  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 ( $K_2O + Na_2O$ ) content from ~ 4.6 to ~ 10 wt.%. All these facies have relatively large ranges in  $Fe_2O_3^{tot}$  (~ 2–10.3

wt.%), MgO (Mg#  $\sim 0.04-0.8$ ), CaO ( $\sim 1.7-10.6$  wt.%), Al<sub>2</sub>O<sub>3</sub> (14.2-16.5 wt.%), TiO<sub>2</sub> ( $\sim$ 308 0.4-2.3 wt.%) and  $P_2O_5$  (~ 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<sub>2</sub>O up to ~ 9 wt.%), suggesting that they might have been affected by general Na-320 metasomatism conditions (Fig. 7c). In terms of volatile element compositions, Cl and 321 SO<sub>3</sub> 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.% SO<sub>3</sub>) (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

## 6. Mineralogy

330 *6.1. Apatite* 

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## 6.1.1. Major element composition

Table 3 shows representative major element analyses of the studied apatites. The two major constituents —i.e., CaO and P<sub>2</sub>O<sub>5</sub>— show rather little variations: CaO and P<sub>2</sub>O<sub>5</sub> vary between 53 and 57 wt.% and between 39 and 44 wt.%, respectively. The 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 (0.67-0.90 wt.%). In contrast, the Anemzi apatites associated with dark gangue (amphibole matrix), are rather heterogeneous: their F contents decrease from core to rim (from ~ 1.9 to ~ 0.8 wt.%) while Cl increases (from ~ 0.6 to ~ 2.5 wt.%) (Table 3). All analyzed Tirrhist-Inouzane apatites have relatively homogeneous F and CI contents (~ 1.9-2.4 and ~ 0.34-0.47 wt.%, respectively). Similarly, the apatites from Tassent and Tasraft (fine gems) have F concentrations between 1.7 and 2.8 wt.% and low to moderate CI contents (0.5–1.47 wt.%). On the other hand, distinct apatite compositions have been yielded by amphibole-bearing apatites from both Tasraft and Ait Daoud-Toumliline: the first ones show compositions intermediate between those of Cl-rich apatites and those of CI-F apatites (F contents vary between 0.47 and 1.47 wt.% and CI between 3.44 and 1.5 wt.%); the second ones are Cl-rich apatites with high Cl (up to 3.3 wt.%) and low F (~ 0.6-1 wt.%) contents. If we considered all apatites analyses, they show a good linear trend and progressive compositional variations from the F-rich to Clrich apatites as shown by Fig 8a.

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In all studied apatites, the element substitutions are always very low, and they vary between the different apatite deposits and even between the crystals of the same deposit (see Table 3 and Figs. 8b, c, d). The major substituent element is Si (0.1 < SiO<sub>2</sub>) wt.% < 0.8). Na<sub>2</sub>O contents can reach 0.55 wt.%, whereas FeO<sup>tot</sup> and MgO never exceed 0.11 and 0.08 wt.%, respectively. The S contents are particularly variable: SO<sub>2</sub> varies between 0 and 0.57 wt.%. In detail, the amphibole-bearing apatites from Ait Daoud-Toumiline and Tasraft show guite similar compositions with relatively high Na<sub>2</sub>O and MgO contents (up to 0.57 wt.% and 0.9 wt.%, respectively), FeOtot contents between 0.04 and 0.11 wt.% and low concentrations of SiO<sub>2</sub> (< 0.4 wt.%) and SO<sub>2</sub> (~ 0-0.3 wt.%). Similar FeOtot and SiO<sub>2</sub> abundances (0.04–0.10 wt.% and 0.18–0.40 wt.%, respectively) have been measured in Tassent apatite but with generally low Na<sub>2</sub>O (0.06-0.29 wt.%) and SO<sub>2</sub> (< 0.04 wt.%) contents and no MgO. The apatites from Tirrhist-Inouzane and Tasraft (fine gems) have MgO below detection limit and they generally contain similar low Na<sub>2</sub>O (≤ 0.08 wt.%) and FeO<sup>tot</sup> (≤ 0.04 wt.%) concentrations, whereas SiO<sub>2</sub> (up to 0.76 wt.%) and SO<sub>2</sub> (0.30–0.57 wt.%) abundances are relatively high. The Anemzi apatites from both white and dark gangues have comparable Na<sub>2</sub>O (0-0.15 wt.%), MgO ( $\leq$  0.01 wt.%) and FeO <sup>tot</sup> (0.02-0.09 wt.%) concentrations. However, these two types of apatite are distinguished by their SiO<sub>2</sub> and SO<sub>2</sub> contents: the apatites from the dark gangue have SiO<sub>2</sub> (0.12–0.32 wt.%) and SO<sub>2</sub> (0–0.04 wt.%) significantly lower than those of the white gangue apatites (0.62–0.70 and 0.01–0.42 wt.%, respectively).

In addition, the rim-core chemical variations (e.g., SiO<sub>2</sub>, FeO<sup>tot</sup>, Na<sub>2</sub>O, Cl, 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 SO<sub>2</sub> contents decrease from core to rim while Na<sub>2</sub>O contents increase (Table 3).

To further constrain the relationships between the apatites and their magmatic host rocks, the apatites in Tirrhist-Inouzane syenites have also been analyzed (see Table 3). These igneous apatite grains have similar compositions compared to the Tirrhist-Inouzane, Anemzi (white gangue), Tassent and Tasraft (fine gems) apatite crystals in veins in terms of F (2–2.3 wt.%), CI (0.5–0.8 wt.%), Na<sub>2</sub>O (0.1–0.19 wt.%), MgO (< 0.01) and FeO<sup>tot</sup> (0.04–0.09 wt.%), and they are clearly distinguished from both 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<sub>2</sub> and SO<sub>2</sub> abundances in the syenite apatites are similar to those found in the gemmy apatites in veins from Tassent and Anemzi (dark gangue) (SO<sub>2</sub> <0.04 wt.%, SiO<sub>2</sub> ~ 0.35 wt.%) (Fig. 8d).

## 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

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

The V contents of apatites vary greatly between the different deposits. They are very low (between 3 and 4 ppm) in the Tassent apatites and slightly higher (between 18 and 34 ppm) in the Tirrhist-Inouzane and high in Ait Daoud-Toumliline (55-77 ppm) (Fig. 9a). We also find these high values but with variability in both Tasraft apatite types: 3–128 ppm in the amphibole-bearing apatites and 96–146 ppm in the fine apatite gems. 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 they can even reach high values (0.17-128 ppm) as in Tasraft. The Mn contents are 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 latter values are relatively close to that found in the Tassent apatites (222-241 ppm Mn). The two types of apatite from Tasraft have Mn contents significantly different: 63– 96 ppm for the fine gem-crystals and 138-250 ppm for the Amp-bearing crystals. The Mn contents of the apatites from Tirrhist-Inouzane (140-148 ppm) and Ait Daoud-Toumliline (116-131)homogeneous and quite similar. Strontium ppm) are

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

In addition, if we considered all apatites analyses from all studied veins, they show a rough positive correlation between total REE and Na<sub>2</sub>O from the less to more CI-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).

## 6.2. The gangue minerals

## 6.2.1. Clinopyroxene

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Clinopyroxene is exclusively observed in the F-rich apatites veins (e.g., Figs. 3, 4 and 6). The crystals are euhedral, up to 3 cm in size and dark to light green in color, sometimes with well-marked zoning corresponding to an alternation of dark and light green domains. Dark and light green grains also occur in almost all magmatic rocks hosting the apatite veins: they appear as euhedral to subhedral grains (0.5 and 2 mm, Figs. 3-4, 6). Major and trace element abundances of clinopyroxenes are given in Tables 4–5. The two major constituents —i.e., SiO<sub>2</sub> and CaO— show little variations; the representative values are ~ 49-54 wt.% SiO<sub>2</sub> and 20-26 wt.% CaO. In detail, all analyzed dark green clinopyroxene zones and crystals from both apatite-bearing veins and country alkaline rocks are similar and have hedenbergite to Fe-rich augite compositions (Wo<sub>44-49</sub>, En<sub>12-26</sub>, Fs<sub>27-43</sub>, see Fig. 13a and Table 4; e.g., Morimoto et al., 1988) with low Mg# [Mg/(Mg + Fe<sup>2+</sup>)  $\sim$  0.32–0.66], high total FeO content ( $\sim$  16–23 wt. %), and moderate to high Na<sub>2</sub>O values (up to  $\sim$  3 wt. %) and MnO (up to 1.4 wt. %). However, the light green zones and crystals, are mainly diopside in compositions (Wo<sub>46-</sub>  $_{51}$ , En<sub>27-41</sub>, Fs<sub>8-25</sub>) with high Mg# ~ (up to 0.95), and low total FeO content (~ 5–14 wt. %), MnO ( $\sim 0.1-0.4$  wt. %) and Na<sub>2</sub>O values (mostly < 2 wt. %). All these clinopyroxene types have similar variable compositional range, with, Al<sub>2</sub>O<sub>3</sub> (~ 0.1–2.6 wt. %), TiO<sub>2</sub> (mostly < 1 wt. %) and  $Cr_2O_3$  (0–0.07 wt. %) contents.

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

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

## 6.2.2. Amphibole

Amphibole occurs as main gangue mineral in Cl-rich apatites veins (e.g., Ait-Daoud-Toumliline; Fig. 5) and as inclusions in almost all the Cl-rich apatites (e.g., Ait Daoud-Toumliline, Tasraft and Anemzi; Figs. 2, 5–6). It forms euhedral and acicular green to brown crystals up to 2 cm in size. Amphibole also occurs as euhedral to 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 element compositions of the amphiboles. All amphiboles from apatite veins and their 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 ~ 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 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 abundances have been analyzed for Anemzi apatite veins (dark gangue) and are given 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<sub>n</sub>/Yb<sub>n</sub> ~ 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).

#### 6.2.3. Feldspars

Feldspars are commonly present in all studied vein-type apatite ores. Table 6 displays representative feldspar analyses. In all apatite ores and magmatic host rocks (Figs. 2–6), albite is the most abundant feldspar: the crystals are euhedral to subhedral and of centimeter size (up to 5 cm). Their compositions are similar, and they correspond almost pure to albite (Ab  $\sim$  90 to 100). K-feldspar is also present but less abundant than 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 are between Or<sub>94</sub> and Or<sub>99</sub>. Anorthoclase compositions (Ab  $\sim$  70–75, An  $\sim$  1–3, Or  $\sim$  23–29) are exclusively found in the magmatic host rocks (see Table 6).

#### 6.2.4. Other minerals

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

about ~ 91–95 wt.% in the apatite veins. In the magmatic host rock, the magnetite composition varies from magnetite (FeO<sup>tot</sup> ~ 90–95 wt.%) to Ti-magnetite [FeO<sup>tot</sup> ~ 87 wt.% and TiO<sub>2</sub> ~ 3 wt.%], sometimes with ilmenite exsolutions (TiO<sub>2</sub> ~ 45–54 wt.% and FeO<sup>tot</sup> ~ 46–50 wt.%) (Table 7).

Titanite is also present in both apatite veins and host rocks and the analyses are reported in Table 7. It is associated with apatite veins and forms greenish yellow euhedral crystals up to 2 cm in size; in magmatic host rocks, it occurs as dark brown to colorless euhedral to subhedral crystals (0.5–2 mm). Titanite from veins has relatively homogeneous contents in SiO<sub>2</sub>, TiO<sub>2</sub>, and CaO (~ 29.5, ~ 41.5 and 29 wt.% respectively), whereas in the host rocks the titanite compositions are more variable: 20–32 wt.% SiO<sub>2</sub>, 29–54 wt.% TiO<sub>2</sub> and 19–29 wt.% CaO. On the other hand, rutile is observed and analyzed exclusively in the magmatic host rock, forming small euhedral to suhedral dark-red grains (up to 0.2 mm in size) and its analyses are also given in Table 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 SiO<sub>2</sub> wt.%, 18.50–22.70 Al<sub>2</sub>O<sub>3</sub> wt.%, 21–25 CaO wt% wt.%, with slight variation FeO<sup>tot</sup> content (~ 10–18 wt.%).

Prehnite is observed in the Tassent and Ait Daoud-Toumliline apatite mineralized 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.

## 7. Discussion and conclusions

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According to our field observations, and petrological, mineralogical, and geochemical study, all Moroccan Central High-Atlas vein-type apatite ores (mostly gemquality) are hosted by differentiated igneous intrusions ranging from syenite-quartz monzonite (dominant) to monzodiorite-gabbrodiorite (Fig. 7 and Table 2). The spatial association with Mesozoic (Jurassic-Cretaceous) alkaline/transitional rocks is typical of phosphates derived from silicate alkaline-carbonatite complexes (e.g., Simandl and Paradis, 2018 and references therein). However, carbonatites have not been found in the studied area, although the ore bodies are not so far to the well-known Tamazeght Eocene carbonatite complex (see Fig. 1b). Our new data lead us to distinguish two types of apatite ores: (i) high gem-quality F-rich apatites associated with clinopyroxene (diopside to hedenbergite-augite) and (ii) gemmy Cl-rich apatites mainly formed in an amphibole matrix (hornblende-edenite to actinolite) (Figs. 2-6, 8, Table 3). Both ore bodies are also associated with feldspars (albitic plagioclase dominant and orthoclase), quartz, magnetite, titanite, epidote, calcite, and prehnite. All studied apatites of both deposit types have similar REE and multi-trace element patterns which suggest that they could have a relatively close origin (Figs. 9, 10, 11, Table 3). A comparison between the Central High-Atlas apatites and those of

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the well-known Sweden Kiruna-type iron ores which formed by late-stage of magmatic differentiation of felsic magmas (pink field in Fig. 10; data from Frietsch and Perdahl, 1995) shows that the REE compositions of apatites from both deposits are similar with pronounced negative Eu anomaly. Conversely, they differ from the REE patterns of the worldwide carbonatite apatites from the Oka (Canada), Kaiserstuhl (Germany), Jacupiranga (Brazil), Fen (Norway), Sokli (Finland), Hörningsholmen-Alnö (Sweden), Siilinjärvi (Finnland) and Loolekop-Phalaborwa (South Africa) complexes (green field in Fig. 10; data from Ingrid, 1998; Chen and Simonetti, 2013; Doroshkevich et al., 2018; 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 High-Atlas apatites studied strongly suggests that feldspar crystallized from phosphaterich melt prior to apatite crystallization. Such negative Eu anomalies in apatite have also been reported in fenites (Eu/Eu\* ~ 0.73-0.84, e.g., Decrée et al., 2020) as a result of cooling and crystallization of carbonatitic and alkaline magmas in the crust and the presence of alkali-rich fluids that metasomatize the surrounding country rocks (e.g., Elliott et al., 2018 and references therein). Although many of the mineralogical features 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 metasomatism affecting the magmatic country rocks (Fig. 7) suggest that fenitization 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 contents (Fig. 14a-b; Belousova et al., 2002) strongly indicate that Central High-Atlas apatites are co-genetic and chemically similar to the magmatic apatites of granitoids of

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Kiruna type iron ores (Fig. 14a-b). Indeed, the mineralogical and geochemical signature of the Central High-Atlas apatite vein-type ores may be related to host-alkaline magma crystallization and evolution rather than carbonatite magma. These observations are corroborated by apatite discrimination diagrams based on the concentrations of several trace elements in apatite (Figs. 14c-d; Mao et al. 2016), showing that the Central High-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 systems are clearly interpreted as origin from magmatic hydrothermal systems (mainly 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 be largely linked to the Central High-Atlas differentiated magmatic rocks (mostly syenites) (Figs. 9, 10, 11, 12, 14). Plagioclases in both veins and host-rocks indicate that both derived from sodic-rich melt or/and underwent general albitization (see above and Table 6, Fig. 7b-c). The clinopyroxene and amphibole observed in both units (veins and host rocks) refer both to Ca-rich minerals and support a common igneous origin (Table 4-5 and Fig. 13). Altogether, field observations and mineralogical and 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 of differentiated rock (likely syenites), although hydrothermal/continental contamination 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

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

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

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# Figure captions

922

- 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-
- 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.
- 928 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
- 931 (Mag), quartz (Qz), amphibole (Amp).
- Fig. 3. (a, b) Hand specimen and (c, e, f, d) microscopic photographs of the Tirrhist-
- 933 Inouzane apatite mineralization showing gangue- and host rock-forming minerals.
- 934 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),
- 937 titanite (Ttn).
- 938 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.

- 940 Fig. 6. (a) Amphibole-bearing apatite gem in mount, (b) hand specimen and (c, d, e)
- 941 microscopic photographs of the Tasraft apatite mineralization (fine gems), showing
- 942 gangue- and host rock-forming minerals.
- 943 Fig. 7. Chemical classification for the lithologies hosting the Central High-Atlas vein-
- type apatite deposits. (a) TAS classification diagram (Middlemost, 1994). (b) K<sub>2</sub>O vs.
- SiO<sub>2</sub> diagram of Rickwood (1989). (c)  $(K_2O+Na_2O)$  vs.  $[K_2O/(K_2O+Na_2O)]*100$  plot (after
- 946 Hughes, 1973). Literature data compiled from Armando (1999), Lhachmi et al. (2001),
- 2018). Zayane et al. (2002) and Essaifi and Zayane (2018).
- 948 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
- 950 corresponding to locations of these profiles.
- 951 Fig. 9. Compositional variation diagrams for the most abundant trace elements in
- 952 Central High-Atlas apatites.
- 953 **Fig. 10.** REE patterns normalized to chondrites (McDonough and Sun, 1995) for the
- 954 Central High-Atlas apatites. Worldwide carbonatite apatite data are from Ingrid (1998),
- 955 Chen and Simonetti (2013), Doroshkevich et al. (2018) and Decrée et al. (2020). Iron
- ore apatite data are from Frietsch and Perdahl (1995).
- 957 **Fig. 11.** Spider diagrams normalized to chondrites (McDonough and Sun, 1995) for the
- 958 Central High-Atlas apatites.
- 959 **Fig. 12.** ΣREE (ppm) versus Na<sub>2</sub>O 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  $0.963\log U + 6.589$ ]. **DP1-2** [=  $0.2073\log Mn - 1.035\log Sr + 15.1\log Y + 4.995\log La - 1.035\log Sr + 1.035\log Sr$ 5.804logCe + 0.1741logEu - 8.771logDy - 4.326logYb + 2.022logPb - 0.6719logTh + 971  $0.02096\log U - 10.45$ ]. **DP4-1** [=  $5.379 \cdot \log V + 1.0285 \cdot \log Mn + 1.0004 \cdot \log Sr - 1.0004 \cdot \log Mn$ 972  $0.0447 \cdot \log \text{Ce} + 3.169 \cdot \log \text{Eu} - 5.412 \cdot \log \text{Yb} - 0.3302 \cdot \log \text{Pb} - 0.1080 \cdot \log \text{Th} + 5.385$ ]. 973
- Fig. 15. A schematic model for the two main Central High-Atlas vein-type apatite ores.

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