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Multiphase magma intrusion, ore-enhancement and hydrothermal carbonatisation in the Siah-Kamar porphyry Mo deposit, Urumieh-Dokhtar magmatic zone, NW Iran

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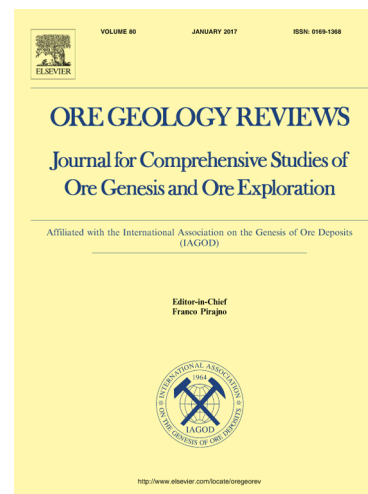
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1 **Multiphase magma intrusion, ore-enhancement and**

2 **hydrothermal carbonatisation in the Siah-Kamar porphyry Mo**

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35
36 **Abstract**

37 The Siah-Kamar Mo deposit (SKMD) is located at the northwestern termination of the
38 Urumieh-Dokhtar magmatic zone and it is the only porphyry Mo ore reserve in Iran. The
39 exploration program documented 39.2 Mt proved reserves @ 539 ppm Mo and 66.4 Mt
40 probable reserves @ 266 ppm Mo. In this study, field and petrographic investigations,
41 integrated with geochemical (fluid inclusion and quartz chemistry) and geochronological (U-
42 Pb zircon, Re-Os molybdenite, and Rb-Sr multimineral isochron) studies are used to propose
43 a metallogenic model for the Mo mineralisation in the SKMD. The geology of the SKMD is
44 characterized by the emplacement of a multiphase Oligocene basic/intermediate (at ca. 33-30
45 Ma) to acidic (29-28 Ma) magmatic suite, which intruded the Eocene volcanic country rocks.
46 The alteration zone, about 4×3 km in size and with a general NW-SE trend, is centered
47 within the main basic porphyry stock, grading from an inner potassic-sodic zone to peripheral
48 phyllic/propylitic halos. The late acidic magmatic products (stocks and dykes) intruded and
49 post-dated the main alteration zone. Two-stage Mo mineralisation is recognised, including:
50 (i) stage-1, disseminated molybdenite, coeval with the formation of potassic-sodic alteration
51 and minor, microscale Fsp, Bt, Qz+Po veinlets; and (ii) stage-2, high-grade
52 molybdenite+carbonate (± sericite), structurally-controlled stockwork veining. Fluid
53 inclusion systematics combined with TitaniQ thermometry documents a mineralising fluid
54 system compatible with a transition from high-temperature (up to ca. 600 °C) magmatic to
55 epithermal (250 °C) conditions during progressive cooling, exhumation and mixing with
56 meteoric sources at shallow crustal conditions (ca. 7-3 km). The Re-Os molybdenite dating
57 constrains the high-grade Mo ore formation at ca. 29-28 Ma, attesting for the intimate linkage
58 between the main Mo mineralisation and the acidic magmatic phase in the area. The Rb-Sr
59 geochronology of the potassic-sodic alteration zones confirms the two-stage
60 magmatic/mineralisation scenarios, overlapping within errors with the results obtained from
61 the U-Pb zircon geochronology and constraining the formation of the potassic-sodic and
62 phyllic alteration at ca. 33 and 28 Ma, respectively. Our results document an uncommon
63 scenario of two-stage porphyry Mo mineralisation associated with intensive late stage
64 carbonate precipitation and achieved during a long-lasting and multiphase magmatic pulses
65 of Oligocene age. We highlight the dominant role of acidic fluid neutralisation for further ore
66 enrichment during polyphase magma intrusion as the dominant factor controlling the Mo
67 mineralisation in the SKMD. Comparison at a regional-scale indicates that parameters such
68 as longevity of magma supply, progressive magma crystallization/differentiation, and the

69 presence of a possible pre-enriched crustal material should be considered responsible for the

70 Mo endowment in the UDMZ.

71

72 **Key words**: porphyry Mo, ore deposits, magmatism, fluids, Urumieh-Dokhtar zone, Iran

73

1.   Introduction

75   Molybdenum (Mo) porphyry-type deposits supply the main Mo demands worldwide (>

76 95%) (John and Taylor, 2016). The Mo deposits are mainly associated with subduction-

77 related settings, such as volcano-plutonic magmatic arcs, back-arcs and continental collision

78 orogens (Westra and Keith, 1981; Wallace, 1995; Seedorff et al., 2005; Taylor et al., 2012;

79 Wu et al., 2017). They are mainly located in the western Cordillera of North America (Ayres

80 et al., 1982; Duke, 2007; Kerr et al., 2009), in Eastern Europe (Janković, 1982), Australia

81 (Whitcher, 1975), China (Mao et al., 2008; Zeng et al., 2012; Wu et al., 2017), Russia

82 (Sutulov, 1973), and elsewhere in Asia (Heinhorst et al., 2000).

83   Porphyry molybdenum deposits have been classified based on the Mo modal abundance, F

84 content, geochemical fingerprint of associated magmatism, and geodynamic setting of

85 formation (Westra and Keith, 1981; Ludington et al., 2009; Ludington and Plumlee, 2009;

86 Taylor et al., 2012; Wu et al., 2017). In particular, two end-member porphyry Mo

87 mineralisation types have been proposed in the literature: the Endako- and the Climax-type

88 (Selby and Creaser, 2001). The Endako-type deposits are characterised by low-grade

89 (Mo<0.15 wt.%), but large-tonnage Mo ores and low F (<0.05 wt.%) in a continental arc

90 setting associated with calc-alkaline magmatism. Tungsten may be enriched as a by-product

91 metal, but copper occurs as in minor quantities or is absent (Doebrich et al., 1996; Taylor et

92 al., 2012). The Climax-type deposits are instead characterised by high-grade (Mo>0.15 wt.%)

93 Mo ores and high F (>0.05 wt.%) in an intraplate setting and associated with alkali-calcic and

94 alkali magmatism (Westra and Keith, 1981).

95   The duration of the mineralisation process in porphyry systems commonly ranges from

96 100 k.y. to 1.5 m.y. (Sillitoe, 2010). Based on numerical modelling, Cathles et al. (1997)

97 proposed a lifetime no longer than 800,000 years for a geothermal system of temperatures

98 greater than 200 °C. The long lifetime (> 1 m.y.) of magmatic-hydrothermal activity mainly

99 depends upon volume, emplacement depth, and temperature of magma, conductive and

100 convective cooling, and permeability of the host rocks (Taylor et al., 2012). It is also

101 demonstrated that multiple events of magma intrusion can increase the lifetime of porphyry

102   copper deposits in excess of 1 m.y. (Chiaradia et al., 2009; John et al., 2010). The inter-

103   mineral intrusive pulses can be either mineralizing or barren and, consequently, can enrich or

104   destroy the former mineralized zones (Sillitoe, 2010). In particular, long-lived magmatism

105   and fractionation, together with fluid exsolution and a change toward more reducing and acid

106   conditions in the mineralising environment are recognised as the key factors for the Mo

107   endowment in the residual melts (e.g., Candela and Holland, 1986; Keith et al., 1986; Blevin

108   and Chappell, 1992; Candela, 1992; Audetat et al., 2008; Seo et al., 2012; Wilkinson, 2013;

109   Zhang et al., 2018).

110   The majority of the porphyry Cu–(Mo, Au) deposits in Iran occur along the Cenozoic

111   Urumieh-Dokhtar magmatic zone (UDMZ) and the Arasbaran magmatic zone, including the

112   world-class SarCheshmeh, Sungun, and Meiduk deposits (Asadi et al., 2014; Aghazadeh et

113   al., 2015; Richards and Sholeh, 2016) (Fig. 1 and supplementary material #1). The Siah-

114   Kamar Mo deposit (SKMD) (Nabatian et al., 2017b; Simmonds et al., 2019), located at the

115   northwestern termination of the UDMZ, from Mianeh to Hashtroud cities (Figs. 1 and 2), is

116   the only Mo ore reserve in Iran. Despite the presence of some alteration zones, no porphyry

117   deposits or significant mineralisation has been reported in the area before the exploratory

118   studies carried out by National Iranian Copper Industries Company since 2005 (NICICO,

119   2010). Preliminary exploration on the altered zones has shown a significant Mo-W

120   enrichment, whereas the deposit is barren with respect to Cu and Au. The exploration

121   program held by the owner within the SKMD documented the in-depth mineralisation down

122   to 600 m, with a 39.2 Mt proved reserves @ 539 ppm Mo and 66.4 Mt probable reserves @

123   266 ppm Mo (Aria Kansar Samin Co., 2013).

124   Early research studies focused on the magmatism and mineralisation characteristics of the

125   ore deposit. These studies defined the metaluminous, high-K calc-alkaline to shoshonitic

126   geochemical fingerprint of the magmatism referred to a final stage of Neo-Tethys subduction

127   beneath the Iranian plate (Khaleghi et al., 2013; Nabatian et al., 2017b). These studies also

128   reported low salinity and low-to-moderate temperature magmatic fluids as responsible for the

129   mineralisation (Nabatian et al., 2017b). Contrasting age estimates exist for the timing of the

130   Mo mineralisation at the SKMD and still uncertain is the timing and geological scenario of

131   the Mo mineralisation. Nabatian et al. (2017b) presented molybdenite weighted mean Re-Os

132   age of 41.9 ± 3.6 Ma, whereas Simmonds et al. (2019) reported ages between 28.10 ± 0.15

133   and 29.06 ± 0.20 Ma using the same geochronological technique. Simmonds et al. (2019) also

134   reported early Oligocene U-Pb zircon ages (32.70 ± 0.40 Ma to 30.90 ± 0.40 Ma) from the

135   mineralized body, suggesting mineralization has potentially occurred ~1.5 Ma after the

136   crystallization of the porphyry stock. Moreover, key aspects, such as the longevity of the

137   magmatic porphyry system, the hydrothermal-alteration processes, and the structural control

138   on fluid flow and ore mineralisation were poorly considered.

139   Based on detailed field and petrographic investigations integrated with analytical data

140   (fluid inclusion microthermometry, U-Pb zircon, Re-Os Molybdenite, and Rb-Sr

141   geochronology, quartz geochemistry), this contribution is aimed at (i) defining a genetic

142   model for the Mo mineralisation at the SKMD, and (ii) improving our knowledge of the

143   Cenozoic metallogeny within the UDMZ (Fig 1). Our results document an Oligocene, long-

144   lasting history of magma crystallisation/emplacement/alteration (33-28 Ma), which

145   culminated with Mo stockwork mineralisation at ca. 29-28 Ma. The Mo mineralisation was

146   structurally controlled and caused by ore enhancement during renewed magmatism, which

147   induced metal leaching and deposition in the transition from ductile-to-brittle environments

148   above a cooling and degassing magma. These data are used to propose a genetic

149   mineralisation model for the Mo ore and to discuss implications for the regional ore

150   distribution, and for the Mo mineralisation in porphyry systems in general.

151

152   **2.   Geological Background**

153   The UDMZ (Fig. 1) records prolonged Cenozoic magmatic activity, spanning from the

154   Paleocene to the Quaternary (e.g., Richards et al., 2006; Chiu et al., 2013; Yeganehfar et al.,

155   2013; Heidari et al., 2015; Ahmadian et al., 2016; Heidarzadeh et al., 2017; Hosseini et al.,

156   2017; Sarjoughian and Kananian, 2017; Shahsavari Alavijeh et al., 2017). A main phase of

157   magmatism occurred during the Eocene-Oligocene, synchronous with the magmatic flare-up

158   at regional scale (Stocklin, 1968; Verdel et al., 2011; Chiu et al., 2013; Moghadam et al.,

159   2016).

160   Based on the mineralisation distribution and types along the UDMZ, a southern and a

161   northern region can be recognised. The southern region, also known as the Kerman Belt,

162   extending from the Naeen city to Bazman volcano (Naeen-Bazman volcanic zone, NBMZ in

163   Fig. 1), hosts the dominant and largest porphyry Cu-Mo deposits of Iran, which are mostly

164   Miocene in age (Aghazadeh et al., 2015). Magmatic products show a general calc-alkaline

165   (moderate to high-K) and metaluminous fingerprint, with a pronounced adakitic signature

166   during the Miocene (Shahabpour and Kramers, 1987; Hassanzadeh, 1993; Shafiei et al.,

167   2008; Taghipour et al., 2008; Shafiei et al., 2009; Mirnejad et al., 2011; Asadi et al., 2014).

168   Three metallogenic stages have been proposed by Aghazadeh et al. (2015) within this

169   segment, including late Oligocene (29–27 Ma), middle Miocene (14–11 Ma), and late

170   Miocene (9–6 Ma). The northern region, extending from Urumieh/BostanAbad to

171   Naeen/Anarak cities (Fig. 1; supplementary material #1), instead hosts a few relatively

172   smaller deposits. Within this region, two magmatic zones can be recognised: (i) a volcano-

173   plutonic zone from BostanAbad to Anarak cities (BAMZ in Fig. 1; supplementary material

174   #1), Eocene to Oligocene in age, typified by high-K calc-alkaline and shoshonitic signatures

175   (e.g., granitoid batholiths of Zanjan, Hassanzadeh et al., 2008; Kal-e kafi, Ahmadian et al.,

176   2009; Abhar, Castro et al., 2013; Kuh-e Dom, Sarjoughian and Kananian, 2017) and

177   associated with some small, intrusion-related, polymetallic deposits (Ahmadian et al., 2009;

178   Fazel et al., 2015; Ahmadian et al., 2016); and (ii) an Oligocene-Miocene volcano-plutonic

179   zone from Urumieh to Naeen (UNMZ; in Fig. 1), which is characterized by post-collisional

180   calc-alkaline and high-K calc-alkaline to adakite products (e.g., Richards et al., 2006; Chiu et

181   al., 2013; Yeganehfar et al., 2013; Babazadeh et al., 2017; Ballato et al., 2017b; Sarjoughian

182   and Kananian, 2017) and associated with minor Au-rich Cu (Mo) porphyry (e.g., Dalli, Ayati

183   et al., 2013) and epithermal Au deposits (e.g., Zarshuran, Mehrabi et al., 1999; Muteh, Moritz

184   et al., 2006; SariGunay, Richards et al., 2006). Regarding the Miocene magmatism, Shafiei et

185   al. (2008) suggested syn- and post-collisional thickening and melting of Cu- and sulfur-rich

186   peridotite, near the crust–mantle boundary, as responsible for fertile adakitic magmatism in

187   the southern Urumieh-Dokhtar magmatic zone. In contrast, Haschke et al. (2010) suggested

188   that a syn- or post-collisional Miocene delamination in the northern UDMZ had removed the

189   Cu- and S-enriched metasomatised lithospheric arc-root and, subsequently, prevented the Cu

190   mineralisation during collisional magmatism.

191   The AMZ is adjacent and sub-parallel to the UDMZ, running from the Sabalan

192   volcano to the Jolfa city, probably continuing to Armenia into the lesser Caucasian Magmatic

193   zone (Innocenti et al., 1982; Hassanpour et al., 2014; Simmonds et al., 2017) (Fig. 1). The

194   AMZ boundaries have not been defined yet, although it is normally considered as a segment

195   of the UDMZ. Nonetheless, it has been also considered as a part of western Alborz zone

196   (Nabavi, 1976; Aghanabati, 2004; Moritz et al., 2016; Rolland, 2017). The porphyry Cu (Mo-

197   Au) mineralisation span from Oligocene to early Miocene (e.g., Shahabpour and Kramers,

198   1987; McInnes et al., 2003; Aghazadeh et al., 2015) and it is more intense with respect to the

199   northern region of the UDMZ.

200

3.   Materials and Methods

A multidisciplinary research approach is adopted in this study that includes field work and laboratory analyses. Field work was based on the existing 1:250,000 cartography (Amidi et al., 1987) and addressed to map the main magmatic bodies and the alteration types (Fig. 2). A detailed map at the scale 1: 5000 is produced for describing the alteration zoning and the main ore zones (Fig. 3). Field work and petrographical observation form the basis for the sampling strategy for the laboratory work that includes: (i) fluid inclusion microthermometry, (ii) Raman spectroscopy; (iii) LA-ICPMS trace and rare earth (REE) elements analysis; (iv) zircon U-Pb geochronology; (v) molybdenite Re-Os geochronology; and (vi) multi-mineral Rb-Sr geochronology of the alteration assemblages.

The studied samples are shown in Figure 3 and listed in Table 1, where their location, petrography and analytical methods adopted are detailed. The analytical protocols are described in the Appendix. In the following, mineral abbreviations are after Whitney and Evans (2010).

4.   Geology of the study area and the ore deposit

The SKMD is located within the Mianeh intermountain basin (Heidarzadeh et al., 2017), in-between the Alborz and the AMZ, at the southern margin of the Azerbaijan Block at the tip of the active dextral Tabriz Fault (Figs. 1, 2). The stratigraphy of the area is dominated by a wide exposure of Eocene volcanic rocks, which make-up the country rocks of the SKMD. The Eocene volcanic rocks consist of andesite-basalt and trachy-andesite lava beds and vitric dacitic to andesitic tuff (Amidi et al., 1987) (Fig. 2). These volcanic products are intruded or covered by a composite Cenozoic (Oligocene-Miocene) volcano-plutonic complex (Amidi et al., 1987; Khodabandeh et al., 1999). A variety of intrusive and sub-volcanic rocks with variable geometry and composition occur in the study area, including diorite, monzonite to leuco-granite, and rhyodacite porphyry (Amidi et al., 1987; Khodabandeh et al., 1999). The granular intrusive bodies crop out in the northwest and centre of the study area, generally aligned along a NW-SE orientation (Fig. 2). To the southeast (from Khatoon Abad to Siah-Kamar), an array of E-W to NE-SW striking microgranular and porphyritic felsic stocks and dykes crop out (Fig. 2). Miocene volcanic country rocks consist of tuff and ash layers with interlayered andesitic lava beds. This volcanic succession is covered by upper Miocene continental sedimentary deposits (Upper Red Fm.) that crop out in the northwestern and southwestern sectors of the study area. These deposits are unconformably covered by

7

234 Pliocene-Quaternary continental sedimentary successions (Amidi et al., 1987; Ballato et al.,

235 2017a) (Fig. 2).

236   The ore deposit geology is characterised by a major alteration zone centered on a

237 porphyry-type, composite magmatic complex that, intruded within the Eocene volcanic rocks,

238 hosts the main Mol ore (Figs. 2 to 4). Despite the different alteration types, the magmatic

239 bodies share common textural features consisting of a porphyritic microgranular and/or

240 glassy groundmass, with various proportions of AFs, Pl, and mafic phenocrysts (Cpx and/or

241 Amp) in the primary igneous assemblage (see Table 1 for a detailed description). Based on

242 the estimated modal abundance of the primary igneous mineral components, the rock

243 compositions are andesitoid/basaltoid (Le Maitre et al., 2005). The mineralized porphyry

244 body (samples MN02 and MN03 in Table 1) is the largest stock in deposit area with a NW-

245 trending ellipsoid shape (1800×1300 m). The body experienced intense alteration and in

246 some places the primary texture has been destroyed. Where preserved, the primary rock

247 composition ranges from syenite to monzonite-quartzmonzonite (Nabatian et al., 2017b).

248 Also barren magmatic bodies can be recognised in the area, to the south (sample MN31 in

249 Table 1) and to the north (sample MN65 in Table 1) of the mineralised body, in a continuum

250 from syn-to-post ore stage as documented by the alteration patterns and distribution (see inset

251 in Fig. 3).

252   Based on the mapped outcrops of alteration zones and assuming lateral continuity below

253 the Miocene and Pliocene cover rocks, the reconstruction of the alteration zone shows an

254 ellipsoid shape, with a general NW-SE trend and about 4×3 km of areal extent (Fig. 3). The

255 Mol mineralisation occurs both as minor disseminated within the inner potassic-sodic

256 alteration zone and major focused in Qz-Afs-Cb veins.

257   A suite of acidic subvolcanic products (rhyolitic and dacitoid in composition; samples

258 Mn01 and Mn19 in Table 1) are observed to intrude and post-date the alteration zone. These

259 magmatic rocks show only minor evidence of rock alteration (Fig. 3; Table 1).

260

261 **5.   Alteration types**

262   Alteration zoning grades from potassic-sodic alteration in the centre to adjacent phyllic

263 and peripheral propylitic halos (Fig. 3). In the following, we described the main alteration

264 zones, mineral assemblages and their distribution.

265 ***5.1. Potassic-sodic alteration***

266   The potassic-sodic alteration is observed in the core of the altered zone, with an areal

267   extent of ca. 2.4 km^2 (Figs. 3, 4). The alteration is typified by the mineral assemblage Bt+ Kfs

268   + Ab + Mag + Anh ± Ilm, Ap, Mol. Typical is the occurrence of a secondary spotted texture

269   made of Bt-Mag aggregates, likely overprinting early magmatic layering (Fig. 5a). Secondary

270   anhedral Kfs and Ab aggregates overprint early magmatic Pl (Fig. 5b). Molybdenite typically

271   occurs as disseminated flakes within the alteration matrix (Fig. 5c). Biotite occur as very fine

272   grained, dominantly as disseminated grains but also as irregular curvy vein-like aggregates

273   (Fig. 5d). Magnetite grains occur both as fine-grained disseminated crystals in the

274   groundmass and as inclusion in Kfs (Figs. 5b, e). Minor amount of Ilm is observed as

275   inclusions in Bt (Fig. 5e). Late formed Po veins also occur (Figs. 5d). Stockwork

276   development and partial brecciation are ubiquitous and resulted in diverse vein types (Fig. 5a;

277   see also below).

5.2. Propylitic alteration

279   Propylitic alteration is the largest alteration zone that mainly affects the Eocene volcanic

280   host rocks and the porphyry-type magmatic complex (Figs. 3, 4). The width of the propylitic

281   alteration is at least 1 km, but it suddenly decreases with distance from the porphyry-type

282   magmatic complex. This alteration is typified by the assemblage Ep ± Act ± Cb ± Py with

283   stockwork, disseminated and locally brecciated textures close to the porphyry-type magmatic

284   complex (Fig. 5f).

5.3. Phyllic alteration

286   The phyllic alteration rims the core of the potassic-sodic and the marginal alteration zone.

287   Locally it overprints the inner part of the potassic alteration zone (Figs. 3, 4). The phyllic

288   alteration consists of the assemblage Qz + Mus + Py, which is variable distributed within the

289   alteration zone, usually associated with veining and rock fractures, seldom associated with

290   intensive pyritization (ca. 5- 10 % vol.). Pyrite is typically altered to secondary iron oxide and

291   hydroxide minerals in the uppermost portions of the alteration zone. Intermediate argillic

292   alteration (Sillitoe, 2010) is observed to decorate the damage zone of major faults (Fig. 5g-j).

6.   Veining

294   We documented multistage veining, locally associated with pronounced alteration halos.

295   The vein density is highly variable and commonly decreases toward margins of the alteration

296   zones, where the alteration distribution is mainly influenced by vein distribution and

297   persistence. In particular, the vein volume abruptly interrupts at the boundary between the

298   mineralised porphyry complex and the Eocene volcanic host rocks (Fig. 6a).

299   Azimuth rose diagram generated from the measured cumulative vein strikes reveals a

300   mean E-W orientation, associated with minor NW-SE and N-S ones (Fig. 6b). In the

301   following, a description of the vein texture and assemblages is described for each alteration

302   zone.

303   *6.1.*   *Veins in the potassic-sodic alteration zone*

304   A conceptual scheme of the vein generation at the microscale within the inner potassic-

305   sodic zone is presented in Figure 7. The early veins generation (V1) consists of up to mm-

306   size Bt and minor Qz+Po, Ab+Kfs and Kfs veins, sharing a discontinuous and irregular curvy

307   shape. The Fsp veins are commonly associated with Fsp halos; no evidence of Mol

308   mineralisation is observed. Locally, small (up to 0.5 mm) curvy shapes $Qz \pm Po$ veins are

309   also observed (Fig. 5d).

310   The second generation (V2a) consists of a voluminous, cm-sized, Qz-$Kfs \pm Mol \pm Ab$ non-

311   systematic (stockwork) vein array (Figs. 5a and 8a-c). These veins are characterized by a

312   blocky texture, mainly formed by Qz-Kfs aggregates, commonly associated with minor Mol,

313   Sch, and Rt (Figs. 7 and 8a,c). The overall vein texture suggests syntaxial growth and Mol

314   occurs in equilibrium with Qz (Figs. 7 and 8a,b). Carbonate mineralisation is typified by the

315   early appearance of paraspurite ($Ca_5(SiO_4)_2CO_3$) (Colville and Colville, 1977), and Ank and

316   Sid/Ank in the stage-2 veins, which occurs in the vein suture, likely filling remaining vugs

317   (Fig. 8).

318   The third generation (V2b) corresponds to the main ore stage and is characterised by Cb-

319   Mol veins, associated with minor sericite and pyrite (Fig. 9). The Cb-Mol veins mostly

320   rework the pre-existing Qz-Fsp veins/host rocks contacts, often developed as cross-cutting

321   and inter-granular cracks (Fig. 9 a,b). Locally, brecciation of the early Qz-Fsp veins is

322   observed, associated with massive Mol precipitation that often show rosette texture (Figs.

323   9a). A ribbon appearance is commonly observed in the V2b veins due to alternating variation

324   of Cb minerals (Fig. 9c). It is worth nothing that Cb compositions vary from Cal to

325   Sid/Rds/Ank when in equilibrium with the Mol precipitation (Fig. 9b,c). Muscovite mostly

326   developed at the expenses of pristine Kfs (Fig. 9d).

327   In terms of vein distribution, the overall array of Mol mineralised veins (V2a-V2b) is non-

328   systematic (Fig. 6c). When taking into account the V2b vein array, a more systematic

329   distribution is observed, which cluster along the E-W (dominant) and NS strikes (Fig. 6d).

330   *6.2.*   *Veins in the propylitic alteration zone*

331   The propylitic zone is associated with development of brecciation and veins, close to the

332   porphyry mineralised body and in the distal country rocks, respectively. Brecciation causes

333 fragmentation of the country rocks, cemented by Ep+Act+Cb aggregates. Veins occur as

334 high-angle systematic arrays, striking roughly E-W and N-S (Fig. 6e), and are filled with the

335 same mineralogical assemblage (Ep+Act+Cb).

336 *6.3.   Veins in the phyllic alteration zone*

337   Within the phyllic alteration zone, veins are made of mm-size Qz + Py, associated with

338 sub-mm-size Ms (sericite) halos (Fig. 5g-j). They form non-systematic arrays. Within the

339 higher topographic levels of phyllic alteration, the Py grains are converted to iron oxide and

340 hydroxide minerals.

341

342 **7.   Mo ore mineralisation**

343   Two main stages of Mol mineralisation were recognized either as disseminated or

344 stockwork (Figs. 9 and 10). Stage-1 (Mol-I) occurs as disseminated Mol flakes within the

345 porphyry body, in association with the potassic-sodic alteration (Fig. 5c). Stage-2 can be

346 subdivided in two Mol formation events (stage-2a and -2b in Figs. 9 and 10), Mol-II and

347 Mol-III, respectively. Mol-II occurs during V2a formation, in association with minor Sch and

348 Rt. Mol-III is the high-grade ore stage during the Cb V2b formation, beginning with

349 paraspurite and continuing with Fe-Mn Cb mineralisation. Minor amount of Py and

350 secondary Ms (sericite) are associated with the Mol-III precipitation.

351

352 **8.   Quartz chemistry and Ti-in quartz thermometry**

353   Quartz crystals from V2a veins from the potassic-sodic alteration zone were analyzed by

354 in situ LA-ICP-MS for Ti content (16 grains) and trace elements (7 grains). Results are

355 presented in Table 2 and 3, respectively. Analytical details are provided in the Appendix.

356   Analyzed quartz show high Ti (17.4-54.7 ppm) and Al (35.9-160.2 ppm), with significant

357 enrichment in Li (1.9-28.0 ppm) and Ge (0.9-2.0 ppm). In the Al vs. Li diagram, the analysed

358 quartz grains show positive correlation and fall near the 1:1 Al/Li molar ratio line, which is

359 indicative of magmatic and hydrothermal quartz (Dennen, 1966; Müller et al., 2018). In the

360 Al vs. Ge diagram, the quartz compositions are compatible with those from hydrothermal

361 quartz and the Ti contents are typical of quartz veins from (Mo-Cu-Au)-porphyry-type

362 deposits (e.g., Müller et al., 2018) (Fig. 11).

363   The TitaniQ thermometry (Wark and Watson, 2006; revised by Huang and Audétat, 2012),

364 assuming a $aTiO_2 = 1$ for rutile-present conditions provides temperature estimates of 479-575

365 $\pm$ 50 °C and 568-675 $\pm$ 50 °C at 0.5 and 2.5 kbar, respectively.

366

9. Fluid-Inclusion Study

9.1. Petrography

369   Samples from (i) Qz-Fsp V2a and Cb-Mol V2b veins from the potassic-sodic alteration
370   zone (Fig 9a) and (ii) Qz-Py-Ms veins from the phyllic alteration zone (Fig. 5i) were studied
371   for fluid inclusions (FI) analysis in order to assess the chemical-physical properties of the
372   mineralising fluid(s). FI were measured both in quartz and paraspurite from the same vein
373   assemblage, considered as representative of the main Mol mineralisation stages.

374   Based on the observed phases at room temperature, two main types of aqueous FI were
375   recognised following the classification proposed by Roedder (1984): (i) dominant type-A (L-
376   rich + V); and (ii) minor, solid-bearing, type-B (L-rich + V + solid). Type-A is subdivided
377   into four sub-groups based on the alteration zone, host mineral and the V to L volume ratio,
378   from A1 to A4. A summary of FI characteristics and results are given in Table 4. The various
379   identified FI types in this study are briefly described below. Type-A1 and A2 are L-rich + V
380   FI, found within V2a quartz grains in the potassic-sodic alteration zone with the V to L ratios
381   from 0.5 to 1 and from 0.1 to 0.4, respectively. Type-A3 are L-rich + V FI. They are the only
382   detected FI inside quartz crystals from Qz+Py+Ser veins within phyllic alteration zone. Type-
383   A4 are L-rich + V FI from V2b paraspurite crystals within the potassic-sodic alteration zone.

384   Type-A1 are mostly found as solitary or randomly distributed in well-protected Qz grains
385   form post entrapment shearing, and have regular to subhedral geometry, large size (ranging
386   15-100 μm). They occasionally show negative crystal shape, and possess the highest V to L
387   ratios (Fig 12a). Type-A2 FIs are characterized by small sizes (5 to 20 μm), regular with
388   negative crystal shape to irregular geometry (Fig 12b). Type-A3 are very similar to type-A2
389   FI, but with smaller sizes (ranging 5 to 10 μm). They have regular to irregular shapes, some
390   showing negative crystal shapes and their V to L ratios range from 0.2 to 0.4 (Fig 12c). Type-
391   A4 occur along the cleavages of the host crystal, showing irregular and elongated geometry
392   with sizes range 5-20 μm. The V to L ratios range from 0.1 to 0.25, but commonly are below
393   0.15 (Fig 12d).

394   Type-B are solid-bearing L-rich + V FI, rarely found in the cores of V2a quartz grains (Fig
395   12e). They occur mainly isolated and in confined trails that are interpreted to be quartz
396   growth lines. Their sizes range 15-30 μm and mostly have irregular geometry. Their V to L
397   ratios range from 0.1 to 0.2.

9.2. Raman Spectroscopy

12

399   Raman spectroscopy was utilized to define the composition of V and L phases of the type-

400   A FI. For the types-A1 and A4 FI, the obtained spectra for the L and V phase revealed water

401   and water vapor as the major components, respectively (Fig 13). In addition, the L phase of

402   type-A1 FI also showed a clear peak for CO_2 (at 1384 cm^{-1}) in solution (Fig 13a). Other

403   peaks were too weak and not identified. In the V phase of type-A1 FI, apart from water

404   vapor, the only detected gas component is CO_2 (Fermi doublet at 1285 and 1388 cm^{-1}). A

405   weak peak belonging to CO_3^{2-} (1064 cm^{-1}) was also detected (Fig 13b).

406   The results from paraspurite-hosted type-A4 FI were not so clear due to the strong

407   fluorescence of the hosting mineral. No evidence of gases were detected.

9.3.   *Microthermometry*

409   A summary of the FI micro thermometric data is reported in Table 4 and histograms of

410   salinity and T_h are illustrated in Figure 14. All the FI types homogenized to L. The eutectic

411   temperatures (T_e) for the type-A1 FI range -30 to -22.5 °C (mean of -25.3 °C), which are

412   higher than eutectic temperature for the H_2O-NaCl system (Bodnar, 1993). The minimum

413   recorded Te could be considered as the ternary eutectic point temperature (-23 °C) of the

414   H_2O-NaCl-KCl system (Hall et al., 1988). Since minor amounts of CO_3^{2-} was detected by

415   Raman spectroscopy studies inside type-A1 FI, the higher recorded T_e values could be

416   explained by the presence of variable amounts of other components, such as Na_2CO_3

417   (K_2CO_3?) in addition to NaCl and KCl. The final ice-melting (T_{m-ice}) temperatures range from

418   -3.7 to -0.6 °C ($n = 44$), which corresponds to salinities between 6.85 and 1 wt.% NaCl eq.

419   (with a mode of 3.85 wt.% NaCl eq). Type-A1 shows the highest homogenisation

420   temperature (T_h) estimates, ranging 298-365 °C and a well-defined mode at 340 °C (mean

421   value of 333 °C). These values are similar to those obtained by Nabatian et al. (2017b) on the

422   same FI type.

423   The T_e for the type-A2 FI range -31.5 to -23°C, with a mode at -23 °C, compatible with

424   the ternary eutectic point temperature of the H_2O-NaCl-KCl system (Hall et al., 1988). The

425   higher recorded values suggest the presence of other components as for type-A1. The T_{m-ice}

426   ranges from -3.7 to -0.1 °C ($n = 195$), which correspond to salinities between 6.0 and 0.18

427   wt.% NaCl eq., with a mean of 2.6 wt.% NaCl eq.. The T_h values distribute almost

428   homogeneously in a wide range from 170 to 352 °C, with a mean at 272°C.

429   Due to the small size of type-A3 FI, the T_e were measured only in two cases, which

430   provided -22 and -21 °C, respectively. The obtained values are close to the eutectic point

431   temperature of H_2O-NaCl system. The T_{m-ice} ranges from -2.6 to -1 °C ($n = 52$), which

432   correspond to salinities between 4.3 and 1.7 wt.% NaCl eq., with a mean of 1.8 wt.% NaCl

13

433 eq. The T_h values range 232-365 °C, but the data are skewed to higher temperatures, with a

434 mode at 310 °C.

435   The T_e for the type-A4 FI range -33 and -24 °C, with a mean of -27 °C. Since these FI are

436 hosted in carbonate minerals, these T_e values can be attributed to the presence of CO_3^{2-} and/or

437 ions such as Ca^{2+}, Mg^{2+}, Fe^{2+} in addition to $H_2O+NaCl$ in the fluid. The T_{m-ice} ranges from -

438 1.2 to -0.1 (n = 91), which correspond to salinities between 2.1 and 0.2 wt.% NaCl eq., with a

439 mean of 0.6 wt.% NaCl eq. The T_h values are distributed in a very wide range, from 145 to

440 300 °C, with a well-defined mode at 225 °C.

441   The salinity estimates for type-B FI were calculated only in four FI from the melting

442 temperature of halite in the liquid phase upon heating. Halite crystals disappeared prior to the

443 bubble in all FI. The calculated salinity estimates range from 30.5 to 32 wt.% NaCl eq. The

444 average T_h spreads between 203 and 320 °C.

445

446 **10.   U-Pb zircon dating of magmatic rocks**

447   The zircon U-Pb geochronological study was carried out on zircon separates as obtained

448 both from the mineralised (sample MN03) and barren magmatic rocks (samples MN01,

449 MN19 and MN31; Fig. 3 and Table 1). Few zircon grains were recovered from the

450 andesitoid/basaltoid rocks (MN03 and MN31), whilst the acidic rocks (MN01 and MN19)

451 provided a large number of grains. Zircons were first investigated through

452 cathodoluminescence (CL), and back scattered electron (BSE) imaging techniques and then

453 analysed in situ LA-ICP-MS system at the university of Nagoya, Japan (see the Appendix for

454 the methodology and). Analytical results are summarized in Table 5.

455 *MN03*

456   Zircons are generally euhedral to subhedral. Zircon grains show short to long prismatic

457 habits (usually >100 μm up to 500 μm), with length/width ratios 2:1 and up to 6:1. Most of

458 the grains appear as nearly homogeneous in BSE images with rare brighter cores. Most of

459 them possess a few continuous longitudinal fractures and apatite and feldspar inclusions are

460 common. The CL images show oscillatory to sector growth zoning (Fig. 15a). The Th/U

461 values are in the range 0.38-6.3 (n = 21; Table 5), compatible with an igneous origin (e.g.,

462 Rubatto, 2002; Kirkland et al., 2015). Despite discordance of some of the spot results due to

463 Pb loss, the majority of the data define a nearly concordant cluster at about 33 Ma. In a Tera-

464 Wasserburg Concordia diagram, an intercept age of 32.8 ± 1.1 Ma is obtained (2σ; MSWD =

465 3.5, n= 13) (Fig. 15b).

466 *MN31*

467   Most of the zircon grains are of small size (50 to 150 μm) and can be classified as type-1

468 subhedral to anhedral and type-2 euhedral crystals. Type-1 shows complex growth zoning

469 with marginal resorption. Type-2 show oscillatory growth zoning (Fig. 15c). The Th/U values

470 range between 0.3 and 2.57, attesting a magmatic origin. Age analyses of type-1 zircons

471 reveals a large spread in apparent $^{206}Pb/^{238}U$ ages from 41.1 ± 1.6 to 2611 ± 70 Ma (Table 5).

472 Type-2 zircons yielded the youngest apparent $^{206}Pb/^{238}U$ ages at ca. 30 Ma, with a Concordia

473 age of 30.4 ± 1.2 Ma (2σ; MSWD = 0.12, n= 2) (Fig. 15d).

474 *MN01*

475   Zircon grains are generally euhedral to subhedral and show short to medium prismatic

476 habits (usually >100 μm up to 250 μm), with length/width ratios of around 2:1. Most of the

477 grains host abundant inclusions of Ap, Fsp, and Qz. The grains show heterogeneous zoning in

478 BSE images with oscillatory and sector growth zoning in CL images. Xenocrystic cores are

479 rarely preserved, and the cores are overgrown by oscillatory and sector zoned rims (Fig. 15e).

480 Th/U values are systematically above 0.4. The majority of the apparent zircon $^{206}Pb/^{238}U$ ages

481 from the growth zoning domains cluster at about 29 Ma, with a few grains providing early

482 Cambrian (ca. 529 Ma) to the Upper Triassic (ca. 220 Ma) ages. A Concordia age of $28.9 \pm$

483 0.4 Ma (2σ, MSWD = 1.2; n=15) is obtained from the Oligocene zircon population (Fig.

484 15f).

485 *MN19*

486   Zircon grains are generally euhedral to subhedral and show short to long prismatic habits

487 (usually >100 μm up to 300 μm), with length/width ration of 2:1 to 3:1. Most of the grains

488 are heterogeneous and inclusion bearing in BSE images and some of them contain

489 xenocrystic cores. In CL images, most of the grains show oscillatory and sector zoning in rim

490 domains (Fig. 15g). The measured Th/U values are higher than 0.4. Most of the spots

491 performed on the growth domains provided concordant ages, with a Concordia age of $28.3 \pm$

492 0.4 Ma (2σ, MSWD = 0.68; n=21) (Fig. 15h).

493

494 **11.   Molybdenite Re-Os geochronology**

495   Two molybdenite-bearing samples were collected from V2b high-grade Mol veins (stage-

496 2b mineralisation) from the core of the potassic alteration zone (Fig. 3 and Table 6) for Re-Os

497 Mol geochronology (see Appendix). The two samples possess similar Re abundances (~19.3

498 and 22.1 ppm), and as they yield very similar Re-Os dates (below) also contain similar ^{187}Os

499   abundances (~12.2 and 13.9 ppb). The two samples yielded similar Re-Os dates of 28.3 ± 0.2

500   and 28.7 ± 0.2 Ma (Table 6). These ages are in excellent agreement with those previously

501   presented for the SKMD (ca. 29 – 28 Ma) by Simmonds et al. (2019), but are in contrast with

502   much older reported Re-Os Mol dates (ca. 42 Ma) by Nabatian et al. (2017b). The Re-Os Mol

503   dating results of this study and those of Simmonds et al. (2019) also overlap with the U-Pb

504   zircon ages (ca. 29-28 Ma) of the acidic magmatic bodies (samples MN01 and MN19) that

505   intrude the main alteration zone (Fig. 3).

506

507   **12.   Rb -Sr geochronology of the alteration zone(s)**

508   Several samples were selected for Rb-Sr geochronology in order to constrain the age of

509   the fluid-driven alteration processes within the SKMD. Only sample MN02 (rock matrix)

510   coming from the inner potassic-sodic alteration zone provided reliable results (see Table 7,

511   Fig. 16). In other samples either Rb/Sr values of minerals like sericite or Kfs were too low to

512   facilitate derivation of useful age information, or samples were affected by supergene

513   alteration. Results for these samples will be reported elsewhere.

514   For sample MN02, the mineral assemblage in the matrix consists of the early-stage

515   alteration products made of Kfs + Bt + Ap with minor amounts of Mol and Qz. Lately formed

516   Ms (sericite) is also documented. We analyzed Bt, two grain size fractions of Kfs, Ap, and

517   two grain size fractions of sericite. The age obtained for the primary assemblage Bt+ 2

518   Kfs+Ap is 33.3 ± 0.9 Ma with a MSWD (mean square weighted deviation) of 0.16,

519   documenting that this sub-assemblage was in perfect Sr-isotopic equilibrium at that time. The

520   late-stage Ms was formed by fluid-rock interaction and most probably grew at the expense of

521   primary Kfs. Linear regression of the Rb-Sr data for 2 Kfs + Ap +2 Ms results in an age of

522   28.5 ± 1.8 Ma (MSWD = 6.3). It appears that there is slight Sr-isotopic disequilibrium

523   between the two different grain size fractions of sericite, which slightly deteriorates the

524   precision of the age but does not affect its accuracy.

525

526   **13.   Discussion**

527   The zircon U-Pb geochronology from the ore-related intrusive bodies points to a

528   multistage magma emplacement in the study area that, based on the petrographic

529   characteristics, can be grouped in two main episodes of magmatism, at 33-30 Ma (basic to

530   intermediate in composition) and at ca. 29-28 Ma (acidic in composition), respectively. The

531   early episode of magmatism is compatible with the early Oligocene U-Pb zircon ages

532   reported in Simmonds et al. (2019) on the same mineralised body.

533   These magmatic episodes are associated with chronologically distinct

534   alteration/mineralisation types, as discriminated by the Rb-Sr multimineral and Re-Os Mol

535   geochronology. In particular, the Rb-Sr geochronology documented an early Bt-Kfs-Ap

536   assemblage at ca. 33 Ma and a subsequent Ms-bearing one at ca. 28 Ma, thus coeval with the

537   early basic and late acidic magmatic episodes, respectively. We can thus infer the two-stage

538   Mo mineralisation as defined by the textures and mineralogical assemblages in the SKMD

539   (Fig. 10) was polyphase and the consequence of : (i) an early low-grade, disseminated-type

540   mineralisation (stage-1) at ca. 33 Ma, associated with the pervasive potassic-sodic alteration

541   during basic to intermediate magmatism; and (ii) a subsequent, high-grade focused stockwork

542   mineralisation (stage-2) at ca. 29-28 Ma, associated with Qz-Fsp veining and subsequent Cb

543   precipitation during acidic magmatism. This evidence suggests a long-lived (at least 4-5 Ma)

544   period of magma production, differentiation and emplacement to sustain the Mo

545   mineralisation episode(s) in the study area.

546   To form an economic porphyry Mo mineralisation, a significant and multiple magma

547   supply and differentiation within a large magma chamber, is needed to endow reasonable

548   quantities of Mo (e.g., Candela and Holland, 1986; Candela, 1992; Robb, 2004; Audétat,

549   2010; Zhang et al., 2018). The lack of Cu mineralisation in the SKMD, which is at odds with

550   the all known porphyry systems along the Urumieh-Dokhtar magmatic zone (supplementary

551   material #1), also supports a scenario of a long-lasting magma crystallisation and

552   differentiation in the chamber(s), which efficiently led to Cu extraction from the melt to the

553   crystallizing marginal zones into sulfide minerals (e.g., Candela and Holland, 1986; Blevin

554   and Chappell, 1992; Candela, 1992; Klemm et al., 2008; Audétat, 2010). The residual melt

555   magma from such a chamber is then expected to show depletion in Cu and relative

556   enrichment in Mo. With progressive crystallization, a more acidic, fluid-rich magma is

557   produced which would be more fertile with respect to Mo (e.g., Candela and Holland, 1986;

558   Candela, 1992; Robb, 2004; Audétat, 2010; Seo et al., 2012).

559   The longevity of magma chamber(s) could be simply related to the amount of primitive

560   magma nesting deep in the crust (Hawkesworth et al., 2000), the water content of the magma

561   that prevented magma to rise to the same crustal levels unlike its drier equivalent (Robb,

562   2004), or input of numerous batches of magmas from the deep crustal melt reservoir (Glazner

563   et al., 2004).

564

565

13.1. Source of the Mo-bearing magma

567   Apparently, there is a good correlation between Re concentration values in Mol and source

568 of the parental magma. In particular, high (hundred ppm) and low (few ppm) Re contents

569 have been reported in many studies and were referred to as mantle- or to crust-derived

570 magmas, respectively (e.g., Stein et al., 2001; Berzina et al., 2005; Mao et al., 2006; Wu et

571 al., 2017). However temperature of Mol deposition (Ishihara, 1988), the alteration type within

572 the same deposit (Newberry, 1979), and the availability of molybdenite could affect the

573 amount of Re concentrations. Furthermore, based on Nd and Sr isotopic studies, Farmer and

574 DePaolo (1984) proposed that the Cu source is in the mantle and the Mo source in preexisting

575 crust. Many studies have also documented that the most fertile sources for syn- and post-

576 collisional porphyry deposits is a subduction-modified lithosphere (Pettke et al., 2010;

577 Richards, 2015).

578   Molybdenite samples from Tertiary porphyry deposits in Iran show a general positive

579 correlation between higher Re concentration and younger ages (Taghipour et al., 2008;

580 Mirnejad et al., 2013; Aghazadeh et al., 2015; Simmonds and Moazzen, 2015; Nabatian et al.,

581 2017a; 2017b). It was therefore proposed that the Neogene magmas along UDMZ were less

582 contaminated by crustal materials (Nabatian et al., 2017b).

583   The Re contents in the molybdenite samples analysed in this study (19-22 ppm), together

584 with those presented in Simmonds et al. (2019), ranging 10-41 ppm, are remarkably lower

585 than all other porphyry Cu-Mo (Au) systems along the Urumieh-Dokhtar magmatic zone,

586 which are typically above 100 ppm (e.g., Aghazadeh et al., 2015). Significant in this regard is

587 the presence of inherited zircons within both the early (dated at 33-30 Ma) mafic to

588 intermediate and late (dated at 29-28 Ma) acidic magmatic rocks cropping out in the

589 mineralised area (Table 5). These inherited zircons also show resorbed and heterogeneous

590 textures (Fig. 15d), compatible with renewed melting and corrosion (Corfu et al., 2003). In

591 this regard, various papers have outlined the dominant role of juvenile lower crust in metal

592 endowment in porphyry Mo (e.g., Berzina et al., 2015; Liu et al., 2015; Zeng et al., 2015;

593 Zhang et al., 2018) and Cu deposits along southern UDMZ (Asadi et al., 2014). We therefore

594 suggest that the molybdenite Re contents from the SKMD most likely derive from a crustally-

595 contaminated mantle sourced magma. This is in line with the calculated initial isotopic Sr

596 composition of ~0.70497 as derived from sample MN02 (Fig. 16) that is indicative of a

597 mantle-derived magma with minor crustal contaminations (Zindler and Hart, 1986).

598

13.2. Structural control on fluid flow and mineralisation

600   The Mo mineralisation SKMD is structurally controlled as documented by the

601 development of a network of polyphase veining. Overall, the vein arrays are non-systematic,

602 as indicated by a nearly radial pattern of jointing within the main alteration zones (Fig. 6b-c),

603 and the Mol abundance in veins (V2a and V2b) decrease significantly when moving from the

604 inner potassic-sodic alteration zone focused on the main intrusive body to the outer Eocene

605 volcanic host rocks (Fig. 3). Similarly, the intensity of the phyllic alteration changes from

606 intense to low when crossing the contact between the mineralised porphyry and the volcanic

607 host rocks. This evidence suggests that the original intrusive contacts constituted a major

608 structural/rheological boundary that likely acted as a permeability barrier for the fluids

609 exsolved from the crystallizing intrusion (e.g., Oliver and Bons, 2001; Rossetti et al., 2007).

610   Significantly, within the ore body the vein array is more systematic in the transition

611 from V2a to V2b mineralisation stages and in the marginal propylitic alteration zone (Fig. 6).

612 In particular, the occurrence of a nearly orthogonal vein set in the potassic-sodic and

613 propylitic alteration zones points to a geological setting dominated by a horizontal biaxial

614 tensile stress field in an extensional regime (vertical maximum principal stress σ_1) and

615 characterized by reversal of the intermediate (σ_2) and minimum (σ_3) principal stress (Rives et

616 al., 1994; Caputo, 1995) between the NS and E-W paleo-directions. Since the main vein

617 strike distribution cluster around the E-W strike (Fig. 6), the regional σ_3 paleo-direction

618 during the main stage of Mol mineralisation is inferred to trend NS. Therefore, a transition

619 from a nearly isotropic stress field to a differential stress regime dominated by a N-S directed

620 σ_3 direction is envisaged. This also suggests a different style of structural control on ore

621 mineralisation, likely controlled by the fluid pressure changes in the mineralising

622 environment: from early hydrofracturing and stockwork vein arrays under supralithostatic

623 fluid pressures conditions to late planar vein arrays formation under sub-lithostatic

624 conditions.

13.3. Fluid evolution and the mineralising environment

626   No information is provided in this study regarding the fluid(s) geochemistry

627 responsible for the main potassic-sodic alteration and associated disseminated stage-1 Mol

628 precipitation. The main products of this stage fluid(s) (as disseminated and micro-vein types)

629 are Kfs+Ab+Bt+Mt+Po, which is the common high-temperature mineral assemblage in the

630 early stages (orthomagmatic) of porphyry systems (e.g., Shinohara et al., 1995; Seedorff et

631   al., 2005; Sinclair, 2007; Sillitoe, 2010), including Mo deposits (e.g., Questa, Bloom, 1981;

632   and Hudson Bay Mountain, Klemm et al., 2008). This is in line with the compositional

633   layering in the porphyry stock (Fig. 5a), which suggests magma degassing close to the

634   carapace of the rising intrusive body (Sinclair, 2007; Lawley et al., 2010). A magmatic origin

635   for this stage-1 fluids is thus tentatively proposed indicated by the ubiquitous unidirectional

636   solidification textures observed in potassic-sodic alteration zone as it proposed at MAX

637   (Lawley et al., 2010) and Henderson (Shannon et al., 1982) porphyry Mo for the early stage

638   fluids (Lawley et al., 2010). The transition from an oxidising to a reducing mineralising

639   environment is attested by the sequential formation of magnetite, to ilmenite and pyrrhotite

640   (Fig. 10), which can be associated to the Mol-I disseminated precipitation.

641   The early ore-bearing fluids (type-A1 and A2 FI) in V2a quartz veins (Mol-II

642   mineralisation) show T_e values (-22.5°C to -33°C) consistent with a H_2O-NaCl-KCl system

643   (Hall et al., 1988), with variable amounts of other cations such as Ca^{2+}, Mg^{2+}. Quartz

644   geochemistry has demonstrated a hydrothermal (magmatic) origin for the mineralising

645   fluid(s) (Fig. 11). The presence of CO_2 in the type-A1 FI may thus indicate an originally low-

646   salinity and low CO_2-bearing magma-derived fluid(s). The association of low saline fluids,

647   usually containing low amounts of CO_2, is common in porphyry Mo deposits, in particular

648   within arc-related Mo deposits, such as Endako (Selby et al., 2000), Thompson Creek (e.g.,

649   Thompson Creek, Hall et al., 1984; Cannivan Gulch, Darling, 1994; Geumeum, Kim et al.,

650   2016), and, apparently, it has no effect on the size or the ore-grade of the deposit (Taylor et

651   al., 2012). Cline and Bodnar (1991, 1994) have demonstrated that when magma

652   crystallization progresses, the released fluid(s) will have less than 10% chlorine

653   concentration. Since we do not have firm evidence of fluid boiling from the FI assemblage,

654   the rare type-B, high saline (up to 32 wt.% NaCl eq.) fluids in FIs can hence be interpreted as

655   magma-sourced saline brines, segregated in the early stages of magma crystallization (Cline

656   and Bodnar, 1991; 1994). Alternatively, fluid boiling could have occurred at deeper levels,

657   predating the Mol mineralization. The vaporization of CO_2 during boiling could have

658   increased the pH, leading to precipitation of Cu from the fluids (Drummond and Ohmoto,

659   1985), whereas Mo remained dissolved in the residual fluids with lower salinity and CO_2

660   content as hydroxyl (H_2MoO_4) and alkali molybdate complexes (Ulrich and Mavrogenes,

661   2008). In addition, boiling and the associated early metal deposition could have consumed the

662   sulphur, increasing further the solubility of Mo in the residual fluids (Xiaoyun, 1989; Ulrich

663   and Mavrogenes, 2008).

664   Fluids from the phyllic alteration zone (type-A3 FI) show no evidence of CO_2 but similar

665   T_h (240-350 °C) and salinity (1.7-4.3 wt.% NaCl eq.). This is comparable with the Endako

666   porphyry Mo deposit, where the fluid chemistry associated with K-feldspar and sericite

667   alteration assemblages show no distinct differences (Selby et al., 2000). A significant

668   contribution of meteoric fluids is inferred due to the absence of CO_2 and the observed lower

669   T_h and salinities. The paragenetic occurrence of Ser (Ms) with Mol+Cb mineralisation (Mol-

670   III mineralisation) highlights the dominant role of neutralisation and cooling of acidic fluids

671   (Hemley and Hunt, 1992; Giggenbach, 1997) caused by percolating meteoric fluids and

672   mixing, which also caused the sulphide precipitation. Moreover, the coincidence of high-

673   grade Mo precipitation with very low salinity type-A4 FI could be explained by the

674   importance of hydroxyl complex (H_2MoO_4, Ulrich and Mavrogenes, 2008) for molybdenum

675   transportation (Candela and Holland, 1986) in temperatures below 300 °C (Xiaoyun, 1989).

676   Since the Mo solubility decreases with increasing salinity (Keppler and Wyllie, 1991), Mo

677   precipitation should have been facilitated by continuous fluid exsolution and mixing,

678   temperature/pressure fluctuations and/or pH changes (Audétat, 2010; Seo et al., 2012).

679   In order to better constrain the thermo-baric environment associated with Mo

680   mineralisation, FI isochores (Fig. 17a) have been constructed using the BULK and ISOC

681   softwares (Bakker, 2003). Isochores were chosen considering representative fluid inclusions

682   for type-A1 (bulk density of 0.599 g/cc) and A-4 (bulk density of 0.826 g/cc) FI. Calculations

683   were based on the equations of state of Zhang and Frantz (1987) for density and Bodnar

684   (1993), Bodnar and Vityk (1994), and Knight and Bodnar (1989) for the bulk composition.

685   The isochores are then combined with the T estimates as derived from the TitaniQ

686   thermometry for pressure correction. For the type-A1, the area in P–T space defined by the

687   intersections of isochores with T estimates is centered at 1.5 ± 0.5 kbar and 580° ± 75°C.

688   Assuming lithostatic pressure conditions, this conforms to paleogeothermal gradient of ca.

689   100 °C/km and a depth of 7.4 km (based on a lithostatic pressure gradient of 27 MPa km^{-1})

690   for the early (V2a stage) mineralisation. This pressure/depth estimates for the mineralising

691   environment is consistent with those reported in many porphyry Mo deposits (Selby et al.,

692   2000; Taylor et al., 2012; Ni et al., 2015). This is also compatible with the marginal

693   magmatic textures (compositional layering) preserved at the roof of the main mineralised

694   body (Fig. 5a). Using the same geothermal gradient and assuming a progressive transition

695   from lithostatic to hydrostatic pressure conditions, the intersection with the type-A4 isochore

696   provides pressure estimates ranging from 0.25 (based on a hydrostatic pressure gradient of 10

697   MPa km^{-1}) to 0.75 kbar in a narrow temperature range of ca. 250 °C. These P-T estimates

21

698   constrain the high-grade Mo mineralisation during the V2b stage at shallower crustal levels

699   (ca. 3 km) during progressive exhumation of the mineralising system (Fig. 17a).

700   When the different FI types are plotted in a Th vs. salinity diagram, there is a

701   significant overlap in the populations of L-rich+V FI. Nonetheless, a general trend of

702   decreasing Th and salinities values from Type-A1, A2 and A3 (hosted by quartz) to type-A4

703   (hosted by paraspurite) FI can be observed (Fig. 17b). Three main groups of FI can be

704   discriminated in the Th vs. salinity diagram: (i) group-1, with the highest mean of Th, that

705   includes all the type-A1 and part of the type-A2 FI; (ii) group-2 that includes the type-A2 FI,

706   with a general trend to lower Th and salinity values; and (iii) group-3, formed by the type-A4

707   FI. Taking into consideration the fluid evolution processes typical of hydrothermal ore

708   deposits depicted in Wilkinson (2001), group-1 is consistent with isothermal mixing and

709   group-2 with meteoric fluid mixing/dilution, respectively. Group-3 is instead consistent with

710   cooling and pressurisation (Fig. 17b-c). This evidence suggests a mineralising system

711   recording the progressive evolution from a closed to an open fluid circulation system,

712   controlled by the progressive transition from a ductile to brittle environment, where rock

713   fracturing has enhanced permeability and meteoric fluids percolation and mixing.

714   *13.4.*   *A model for the Siah Kamar Mo mineralisation*

715   Collectively, our results from the SKMD confirm a Mo mineralisation scenario

716   compatible with an Endako-type porphyry Mo deposit (see also Nabatian et al., 2017b).

717   Nonetheless, our results also point to peculiar characteristics for the SKMD. The main

718   peculiarity of the SKMD is a prolonged history of magma production and emplacement (ca.

719   4-5 Ma). In fact, despite that multiple magma intrusion processes are common in the

720   evolution of porphyry systems, the time lapse from early- to late-stage mineralisation is

721   usually less than 1 m.y. (Sillitoe, 2010; Mercer et al., 2015). Therefore the SKMD can be

722   classified as an uncommon porphyry Mo mineralization, which operated in a time scale of at

723   least 4-5 Ma. Such mineralisation time scales have been reported from giant and large

724   porphyry systems (e.g., Chuquicamata, Correa et al., 2016; and Halasu, Xue et al., 2016).

725   The concurrence of carbonatization and Mol mineralisation is also a peculiar

726   characteristic of the SKMD. Carbonate precipitation is uncommon in porphyry systems

727   (Taylor et al., 2012) and carbonate veins commonly, which occurred in the latest stages, are

728   either barren (e.g., Selby et al., 2000; Seedorff and Einaudi, 2004; Mao et al., 2011; Ni et al.,

729   2015) or with only minor Mo enrichment (e.g., Yang, 2007; Wang et al., 2017; Zhai et al.,

730   2017).

731   Therefore, any model for the formation of the Mo Siah Kamar mineralisation should take

732   into consideration the following constraints: (i) the U-Pb zircon magmatic ages and the Rb-Sr

733   ages of the alteration mineralogy support a two-stage mineralisation process: early (at ca. 33

734   Ma) low-grade disseminated mineralization (stage-1, Mol-I) during potassic-sodic alteration

735   in a reducing environment and subsequent (at ca 28-29 Ma) high-grade stockwork Mo

736   mineralisation (stage-II, Mol-II and Mol-III, as constrained by the Re-Os Mol

737   geochronology) during phyllic alteration; (ii) the two-stage mineralisation is associated with

738   multiphase intrusions and transition from basic to acidic magmatism, in a time lapse of ca. 4-

739   5 Ma; (iii) the mineralising fluid(s) records transition from a magmatic/hydrothermal- to a

740   meteoric-dominated system across a progressive ductile-to-brittle environment (temperature

741   range from ~600 to 250 °C); and (iv) the dominant role of carbonate precipitation and

742   neutralisation of acidic fluids in the Mo mineralisation (Mol+Ser+Cb assemblage) during

743   fluid cooling.

744   Based on the synchronicity (in the time lapse 28-29 Ma) existing between the

745   crystallisation of the acidic dyke and stock at the rims of the mineralised zone (Fig. 3),

746   phyllic alteration and Mo-mineralisation, it is postulated that mineralising fluids were sourced

747   from these acidic intrusives. Nonetheless, these acidic magmatic rocks are Mo-barren. We

748   then propose a model of Mo mineralisation as primarily caused by the re-fertilisation (ore

749   enhancement) induced by the renewed magma supply at 28-29 Ma. The exposed acidic

750   intrusions are considered as the apophyses of a magmatic system likely supported by a

751   voluminous magma chamber at depth, able to sustain highly perturbed geothermal conditions

752   and renewed fluid supply within the early formed potassic-sodic alteration zone formed at ca.

753   33 Ma (Fig. 18). In such a scenario, the mode of fluid exsolution was controlled and

754   modulated by the rheological evolution of the solidifying shell surrounding the cooling

755   magma. At high-temperature conditions (T>600 °C), fluid-rock equilibrium was likely

756   attained and fluids were entrapped in solidifying magma at depth (ca. 7 km). When

757   temperature decreased and brittle deformation prevailed, more fluids were released into the

758   system and interacted with the ground waters (e.g., Giggenbach, 1997). At this stage (T<

759   300°C), the CO_2 dissolved in the fluids became reactive and the release of CO_2 caused

760   acidification of the fluids (Giggenbach and Soto, 1992; Kaszuba et al., 2005; Little and

761   Jackson, 2010) and significant interaction with the country rocks, leading to mineral

762   dissolution and metal leaching (Bandstra and Brantley, 2008; Liu et al., 2012; Kirsch et al.,

763   2014; Lions et al., 2014) from the early-formed potassic-sodic alteration zone. The deposition

764   zone is thus interpreted as zone of fluid mixing with meteoric ground water, when fluid

765 neutralization and temperature drop down leading to the Ms-Cb precipitation and metal (Mol)

766 mineralisation in the system, focused by structurally-controlled pathways assisted by

767 continuous fracturing of the intrusive carapace.

768

13.5.   Correlation at regional scale

770   Similar Eocene-Oligocene high-K calc-alkaline to shoshonitic magmatism as reported

771 from the SKMD (Khaleghi et al., 2013; Nabatian et al., 2017b) has been also reported in

772 many studies along the UDMZ, AMZ, BAMZ, Lesser Caucasus, and the western Alborz

773 (e.g., Aftabi and Atapour, 2000; Ahmadian et al., 2009; Aghazadeh et al., 2010; Sarjoughian

774 et al., 2012; Kananian et al., 2014; Jamali and Mehrabi, 2015) (Fig. 1). Within this context,

775 the SKMD shows the oldest reported ages among the porphyry deposits within the UDMZ

776 (except the Kal-e-Kafi porphyry Cu-Mo deposit, with zircon U-Pb age of 52-50 Ma,

777 Ahmadian et al., 2016), and only two porphyry Cu-Mo-Au deposits have been reported

778 within the same time window including Bondar-e-Hanza (with Mol Re-Os age of 28.4 ± 0.5

779 Ma, Aghazadeh et al., 2015) and Reagan (with zircon U-Pb age of 29.3 ± 0.2 Ma,

780 Hassanzadeh, 1993) (Fig. 1 and supplementary material #1).

781   By contrast, many porphyry Cu-Mo deposits with older (Eocene) and similar (Oligocene)

782 ages have been reported in the AMZ (Haftcheshmeh Cu-Mo, Mol Re-Os age of 28.2-27.1

783 Ma, Aghazadeh et al., 2015) and Lesser Caucasian magmatic zones (Kadjaran Cu-Mo; 27.3–

784 26.4 Ma, Rezeau et al., 2016). Nonetheless, apart from the SKMD, none of these porphyry

785 systems shows Mo as the first commodity. In particular, whereas the Mo/Cu ratio within

786 SKMD is about 1, the coeval porphyry Cu-Mo deposits of Kadjaran, Haftcheshmeh, and Kal-

787 e Kafi show values of about 0.1, which are significantly higher than the Miocene ones

788 (supplementary material #1). The Mo enrichment in the Eocene-Oligocene porphyry systems

789 could be attributed to either to a relatively deeper emplacement level of the metal-bearing

790 magma (Candela, 1986) or to the contribution and re-fertilisation of a preexisting Mo-

791 enriched crustal source (Farmer and DePaolo, 1984; Wan et al., 2018).

792

14.   Conclusions

794   The main results of this study can be summarised as follows:

795 (1) The SKMD developed during a long-lived magmatic and alteration history, spanning

796 from ca. 33 Ma to 29-28 Ma, associated with a diachronous, low- and high-grade Mo

797 mineralisation.

798 (2) Re-fertilisation of an early formed disseminated Mo ore by renewed magmatism and

799 associated magma degassing and fluid exsolution is proposed as the scenario for ore

800 enhancement and, consequently, for high-grade Mo mineralisation.

801 (3) Leaching of metals from the early formed disseminated ore bodies operated by acidic

802 fluids exsolved from the cooling magmas is recognised as the cause of Mo-enrichment in the

803 mineralising fluids.

804 (4) Mixing of magmatic and meteoric fluids during progressive embrittlement (and cooling)

805 of the mineralising environment is considered as the key factor leading to the high-grade Mo

806 ore formation, through progressive neutralisation of the acidic fluids via structurally-

807 controlled carbonation and sericitisation.

808   Comparison at a regional scale indicates that parameters such as longevity of magma

809 supply, progressive magma crystallization/differentiation and the presence of a possible pre-

810 enriched crustal material should be considered for the Mo endowment in the UMDZ.

811

827

828 **APPENDIX:**

829 **Analytical techniques**

830 **LA-ICP-MS quartz trace element geochemistry**

831 Based on petrographic observations (optical and BSE) and mineral chemistry on polished

832 thin-section samples, 16 representative quartz crystals were selected for in situ trace and

833 REEs element analyses, using laser ablation (LA, CETAC LSX-213 laser system) combined

834 with an inductively coupled plasma mass spectrometer (ICP-MS, AGILENT 7700) at Institut

835 für Mineralogie, Universität Stuttgart. The following laser ablation parameters were used:

836 spot diameter 50 μm, 60% laser power (100% = 4 mJ at a spot diameter of 150 μm), 10 Hz

837 laser pulse repetition rate, and a mixed helium and argon gas flow with 500 ml/min and 800

838 ml/min, respectively, serving as carrier of the ablated material.

839 The data acquisition was performed using the Agilent Mass Hunter software (version

840 B.01.01). Each analysis comprised the acquisition of the individual background ion

841 intensities (gas-blank) for roughly 23 s followed by the acquisition of the ion intensities on

842 laser irradiation of the sample spot for roughly 57 s.

843 The method involved monitoring of 18 isotopes (^{7}Li, ^{9}Be, ^{11}B, ^{27}Al, ^{28,29}Si, ^{31}P, ^{44}Ca,

844 ^{47,49}Ti, ^{55}Mn, ^{56,57}Fe, ^{71}Ga, ^{72,73}Ge, ^{75}As, ^{85}Rb, ^{88}Sr; this selection excludes isobaric

845 interferences of isotopes from other elements) using individual integration times of 10 ms.

846 Reference materials were DLH7 and DLH8 glasses from P&H Developments Ltd., and

847 NIST (National Institute of Standards and Technology, USA) 612 and 610 glasses. Certified,

848 recommended and proposed values for these reference materials are from Jochum et al.

849 (2011). The validity of the calibration, data evaluation, and reproducibility were checked

850 with the reference materials Diorite (DRN) and Zinnwaldite (ZW-C) from Service

851 d'Analyses des Roches et des Mineraux du CNRS. Lithium-borate glass disks of both were

852 prepared using 0.6 g of powder of these reference materials and 3.6 g of lithium borate. All

853 elemental concentrations were calculated relative to the silicon elemental concentration as

854 internal standard which was determined from the results of the ^{29}Si isotope. The absolute

855 silicon concentration was previously measured with the EMP. The same spot target was

856 applied for both EMP and LA-ICP-MS. Precision is estimated better than 5%. The software

857 used for calibration and data evaluation was developed by J. Opitz (Massonne et al., 2013;

858 Baggio et al., 2018).

859

Fluid inclusion microthermometry

Samples representative of the different mineralised quartz-carbonate vein sets were prepared as 150- μm-thick doubly polished wafers and petrography studies were carried out with a polarizing microscope to define the types of fluid inclusions, the populations and their genetic relationships. Microthermometric measurements were made utilizing a Linkam THMSG600 freezing– heating stage at the Istituto di Geologia Ambientale e Geoingegneria of CNR at the University of Roma ''La Sapienza''. The systems were calibrated using pure natural CO2 inclusions for low temperatures and synthetic pure water fluid inclusions for high temperatures, respectively. Reproducibility of the triple point of CO_2 at –56.6 °C and pure H_2O critical point at 374 °C were ± 0.3°C and ± 0.5 °C respectively. Low temperature (Te, Tm) data were determined with a 1–5 °C/min rate, whereas high temperature (Th, Tms) data with a heating rate of 5–20°C/min, respectively. Bulk composition and Isochores for various FI types were calculated by BULK and ISOC softwares provided by (Bakker, 2003).

Raman spectroscopy

A HORIBA LabRAM HR Raman spectrometer at the Dipartimento di Scienze, Università degli Studi di Roma Tre, calibrated using a silicon standard, was employed to acquire the Raman spectra. The micro-Raman spectrometer is equipped with a green argon ion laser (532 nm), focused through a 50× and 100× objectives. Optical filters were employed in order to achieve ~2.5 mW at the surface of the glassy interface. The Raman systems were set with 600 T and 1200 T gratings, exposure time 20 s (3 times), confocal hole of 200–500 μm, and slit of 200 μm, and the spatial resolution of the sample surface is ~1 μm (theoretical spatial resolution = 0.61 λ/NA where λ is the wavelength of the laser (532 nm), and NA is the numerical aperture of the microscope objective being used (0.9 for 100×). Raman spectra were acquired over the range from 90 to 2000 cm^{-1}. Reference values from Frezzotti et al. (2012) for common gases inside fluid inclusions and some minerals were used to interpret the obtained spectra. Furthermore, the CrystalSleuth software (http://rruff.info/) was employed to define the accessory minerals.

Zircon U-Pb Geochronology

The zircon U-Pb geochronology study was carried out at the Department of Earth and Environmental Sciences of Nagoya University. Four samples were selected for zircon grains separation. More than 10 kg for each sample were collected and crushed. Only few zircon grains (ca. 30) were found. Some of them were useless due to the small grain size (< 30 □m) or to the strongly fractured crystal structure. Cathodoluminescence (CL) and Back Scatter

893 (BSE) imaging was used first to gather information on the grain texture and internal growth

894 and/or alteration zoning. Zircon grains with intense fracturing and inclusions were avoided.

895 The zircon grains were analyzed by LA-ICP-MS (Agilent 7700XICPMS machine connected

896 with NWR213 (Electro Scientific Industries) laser ablation system (Kouchi et al., 2015). A

897 standard glass (NIST SRM 610) and two zircon standards, named 91500 (1059 Ma,

898 Wiedenbeck et al., 1995) and OD-3 (33.1 Ma, Iwano et al., 2013) were used. Blanks, the

899 zircon standards, and the standard glass were measured at the beginning and ending of each

900 measurement cycle. Eight points were measured in each cycle. The ISOPLOT V4.15

901 software (Ludwig, 2011) was utilized to calculate the Concordia, statistics and to prepare the

902 age plots. Correction for the common Pb was performed using ^{204}Pb intensity (Cox and

903 Wilton, 2006). Most of the results with high common Pb (values more than 20 %) were

904 excluded from calculations.

905 **Molybdenite Re-Os geochronology**

906 Molybdenite grains were isolated from samples and then gently were milled, washed and

907 dried (Selby and Creaser, 2004). Impurities were separated under microscope and about 100

908 mg of pure molybdenite was prepared for each sample with the analytical protocol following

909 that of (Selby and Creaser, 2004). The Re-Os molybdenite analysis were performed in the

910 Laboratory for Sulfide and Source Rock Geochronology and Geochemistry and the Arthur

911 Holmes Laboratory in the Durham Geochemistry Centre at Durham University (UK). In

912 brief, molybdenite samples were dissolved and equilibrated with a known amount of ^{185}Re

913 and isotopically normal Os in inverse aqua regia (2:1 16 N HNO3 and 12 N HCl, 3 mL) at

914 240 °C for 24 h in a Carius-tube. Rhenium and Os were isolated and purified by solvent

915 extraction, microdistillation, and anion exchange chromatography, and analyzed by negative

916 thermal ionization mass spectrometry on a ThermoScientific TRITON mass spectrometer

917 using Faraday collectors. Total procedural blanks for Re and Os 2.5 pg and 0.1 pg,

918 respectively, with an Os blank composition of 0.21 0.02 (n 6), which are insignificant to the

919 Re and Os levels in the analysed samples. Rhenium and Os concentrations, and Re-Os

920 molybdenite date uncertainties are presented at the 2σ level, which includes the uncertainties

921 in Re and Os mass spectrometer measurement, spike and standard Re and Os isotopic

922 compositions, and calibration uncertainties. Because a mixed tracer solution is used,

923 uncertainties in weights of sample and tracer solution do not affect the calculated age, and are

924 not considered. However, sample and tracer solution weight uncertainties are considered in

925 determining the uncertainty in the Re and ^{187}Os concentrations. Uncertainty in the ^{187}Re

926 decay constant (0.35%, Smoliar et al., 1996)) is also considered.

927

928 **Rb-Sr multimineral geochronology**

929   To determine the ages of mineral assemblage crystallization, we employed the Rb-Sr

930 internal mineral isochron approach. Age information mainly is based on the high-Rb/Sr

931 phases muscovite/sericite, and biotite. Mineral separates were prepared following Glodny et

932 al. (2008). Crushing was performed by hand using pestle and mortar combined with repeated

933 sieving, to preserve the original grain sizes of minerals. Rb–Sr isotopic data were acquired at

934 GFZ Potsdam using a Thermo Scientific TRITON thermal ionization mass spectrometer. Sr

935 isotopic compositions were measured in dynamic multi-collection mode. Rb isotope dilution

936 analysis was done in static multi-collection mode. The value obtained for ^{87}Sr/^{86}Sr of the

937 NIST SRM 987 reference material was 0.710255 ± 0.000024 (2σ, n = 23). For age

938 calculation, uncertainties of $\pm 0.005\%$ for ^{87}Sr/^{86}Sr and of $\pm 1.5\%$ for ^{87}Rb/^{86}Sr ratios were

939 assigned to the results. Uncertainties of isotope and age data are quoted at 2σ. The program

940 ISOPLOT/EX 4.15 (Ludwig, 2011) was used for calculating regression lines. Decay

941 constants are those recommended by Villa et al. (2015).

942

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Figures captions

Figure 1: Simplified tectono-geological map of Iran with the main Cu, Au and Mo ore deposits and their ages. Based on maps from the (Huber, 1977), with additional information from (Berberian and King, 1981) and Richards et al. (2012). See also Table 1 for the references for each mineralisation site.

1455   Figure 2: Simplified geological map of Mianeh-Hashtroud region, as derived from field

1456   and remote sensing investigations (modified after Amidi et al., 1987; NICICO, 2009c, b, a).

1457   Figure 3: Top: Geological-alteration map of the Siah-Kamar Mo deposit (see Fig. 3 for

1458   map location). The ellipse indicates the estimated alteration zone. Bottom: Interpretative

1459   geological cross section across the Mo ore deposit, also showing distribution of the main

1460   alteration types. Abbreviations: Ab, Albite; Act, Actinolite; Ap, Apatite; Bt, Biotite, Cal,

1461   Calcite; Chl, Chlorite; Ep, Epidote; ill, Illite. Kal, Kaolinite; Kfs, K-feldspar; Mag,

1462   Magnetite; Or, Orthose, Psp, Paraspurite; Po, Pyrrhotite; Py, Pyrite; Qtz, Quartz; Sch,

1463   Scheelite; Ser, Sericite.

1464   Figure 4: General field view of the Siah-Kamar Mo deposit area (field of view 2.5 km).

1465   The line drawing illustrates the main rock and alteration types. Abbreviations: alt., alteration;

1466   Cb, carbonate; K, Potassic; mp, mineralized basic/intermediate porphyry rocks.

1467   Figure 5: Rock textures and alterations. (a) The textural appearance of the potassic-sodic

1468   alteration within the main mineralised porphyry body in the outcrop. Alteration mineralogy

1469   consists of Bt-Fsp+ Po, Mg assemblage overprinting early igneous phases. (b) potassic-sodic

1470   alteration at the thin section scale (plane polarised light). (c) Back-scattered electron (BSE)

1471   image showing disseminated molybdenite flakes within the secondary feldspar-biotite

1472   assemblage. (d) Biotite veinlets in the potassic-sodic alteration zone overprinted by Kfs-Qz

1473   veins (plane polarised light). (e) BSE image showing early magnetite inclusions in secondary

1474   feldspar and ilmenite inclusions in texturally-late biotite. (f) Brecciated andesite country

1475   rocks and epidote veining within the propylitic alteration zone. (g) General appearance of the

1476   phyllic and argillic alteration zones. (h) Rock slab from phyllic/silicified zones showing the

1477   development of Qz + Py veins with sericitic halos; (i-j) Microtexture of volcanic country rock

1478   within pronounced phyllic alteration made of Qz + Ser + Py assemblage (crossed polars).

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1480   Figure 6: (a) The contact between the mineralised porphyry body and the country rocks.

1481   Note the presence of potassic alteration and intense veining within the porphyry body and

1482   how the veining dies out abruptly across the contact (see also the interpretative line drawing

1483   in the inset). (b) Rose diagram of the cumulative vein strikes as measured within the different

1484   alteration zones. (c) Contour diagram of the cumulative poles to Mo-mineralised veins (V2a

1485   and V2b) within the potassic-sodic alteration zone (Equal area Schmidt net, lower

hemisphere projection). (d) Contour diagram of the poles to (V2b) Cb-Mo veins within the potassic-sodic alteration zone (Equal area Schmidt net, lower hemisphere projection). (e) Contour diagram of the poles to epidote (Ep) veins within the propylitic alteration zone (Equal area Schmidt net, lower hemisphere projection).

Figure 7. Conceptual model for veining and Mo mineralisation within the potassic-sodic alteration zone (see text for further details).

Figure 8. (a) Rock slab of an early Qz-Kfs-Ab V2a vein with V2b Mol-bearing carbonate mineral assemblages growing in pre-existing vugs. Note the marginal K-feldspar + albite selvage. (b) BSE image showing the textural appearance of a V2a Qz-Kfs vein overprinted by a late, post-ore Fe-oxide vein. Molybdenite occurs in the centre of the vein. (c) BSE image showing coexisting scheelite (Sch) and Mol within V2a Qz + Kfs vein.

Figure 9. (a) Rock slabs of composite V2a-V2b veins showing different degree of the textural overprinting operated by the Cb-Mol mineralisation. (b) BSE image showing V2b veining overprinting early V2a Qz, sericite halos and compositional zoning in Cb. (c) BSE image showing a ribbon texture along margins of a V2b vein, attesting episodic Cb-Mol precipitation. (d) BSE image showing the textural overprint operated by the V2b Cb-Mo veining onto pre-existing Qz-Kfs V2a one. Sericite formed after alteration of Kfs. Note the reworking of the Qz grain boundary during V2b veining.

Figure 10: Mineralization stages and their associated mineral assemblages in the SKMD.

Figure 11. Representative discrimination diagrams for quartz chemistry (after Müller et al., 2018) as derived from in situ LA-ICPMS analyses of quartz grains from V2a veins. (a) Li vs Al. (b) Al vs Ge. (c) Al vs Li.

Figure 12: Microphotographs of the fluid inclusions types hosted in V2a-V2b veins. (a) Type A1 (two-phase L-rich) fluid inclusions in Qz (V2a vein). (b) Type A2 (two-phase L-rich) fluid inclusions in Qz (V2a vein). (c) Type A3 (two-phase L-rich) fluid inclusions in Qz-Py vein from the phyllic alteration zone. (d) Type A4 (two-phase L-rich) fluid inclusions in Psp (V2b Vein). Type B solid-bearing fluid inclusions in Qz (V2a vein).

Figure 13. (a) and (b) Representative Raman spectra from fluid and gas phases from types A1 fluid inclusions in Qz from V2a veins.

1515   Figure 14. Histogram of homogenization temperature (Th) (a) and salinity (b) for the

1516   analysed fluid inclusion types.

1517   Figure 15. (a, c, e and g) Cathodoluminescence images from the analysed zircon grains,

1518   with location of the laser spots (circles and relative id numbers in parenthesis) and obtained

1519 $^{206}Pb/^{238}U$ ages (2σ error; Ma). Spots that provided inherited zircon ages are denoted by

1520   dashed circles. (b) Tera-Wasserburg concordia diagram for sample MN03 (d, f, h).

1521   Conventional Concordia diagrams with Concordia ages indicated (2σ error; Ma) for the

1522   MN01, MN19, and MN31 samples. See also Table 5 for the corresponding analytical results.

1523   Fig 16: Mineral data and Rb–Sr age results for sample MN02. Analytical data are given

1524   in Table 7. Grain size is indicated when different grain size fractions were analyzed. Kfs, K-

1525   feldspar.

1526   Figure 17: (a) Calculated Isochores for the representative type-A1 (quartz) and -A4

1527   (paraspurrite) fluid inclusions (BULK and ISOC software; Bakker, 2003), combined with

1528   isopleths as obtained from Ti-in-quartz thermometry. (b) Salinity versus homogenization

1529   temperature (Th) diagram for all the FI types. Dashed arrows indicate the possible fluid

1530   evolution. (c) Schematic diagram showing typical trends in a Th-salinity space for fluid

1531   evolution in hydrothermal ore deposits (after Wilkinson, 2001).

1532   Figure 18: (a) A model for the Mo mineralisation at Siah-kamar framed within a scenario

1533   of long-lived thermal anomaly and magmatism. (a) Stage-1 mineralisation (33Ma).

1534   Emplacement of the basic/intermediate porphyry body with pervasive potassic-sodic

1535   alteration and low-grade disseminated Mo mineralization. (b) Emplacement of a new batch of

1536   acidic magmas (at 29-28 Ma) caused re-fertilisation of the intrusive/cap rock system, with

1537   formation of V2a veining (stage-2a). (c) The main mineralisation stage (29-28 Ma). The

1538   continuous exsolution of acidic, CO2-bearing fluid from the new magma products caused

1539   leaching of the early deposited Mo and, by neutralisation due to the interaction with meteoric

1540   fluids, the high-grade Mo mineralization during structurally-controlled stockwork Cb veining

1541   (stage-2b).

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1543   Table 1. List of the studied samples with their location, petrographical characteristic and

1544   analytical methods adopted.

S	Ro	Rock texture and	Alteration	Locati	Method

amp le	ck Type	petrography	type	on (decimal degree)	EPMA	LA-	Zircon	Mol.	Rb-Sr
M N01	Rh yolitoi d	Porphyritic with microgranular groundmass. Qz (5-10 %), Pl+Kfs (5-10 %) phenocrysts. Groundmass: Qz (20-30 %), KFsp (40-50 %), Pl (10-15 %), Biotite (<5 %).	Weakly phyllic alteration. Qz veins, rare Ser, Py and Fe-oxides	N: 37.41297 E: 47.59745					
M N02 MN 03	A ndesit oid/Ba saltoid (Diorit e to monzo diorite porphy ry)	Porphyritic with microgranular groundmass. Magmatic texture mostly overprinted. Relic Pl (20-30 %) phenocrysts and pseudomorphous secondary aggregates after Cpx (5-10 %).	Strong sodic-potassic alteration. Disseminated secondary fine grained Ab+Kfs+Qtz+ Bt+Mag (40-50%), Qz-Afs-Mol-Cb-Rt-Sch veins (5-10 %)	N: 37.39916 E: 47.59519				*	
M N19	Da citoid	Porphyritic with glassy groundmass. Glass (50-60 %), euhedral to subhedral Pl (20-25 %), Bt (5-7 %), Amph (2-3 %), Qz (5-7 %) phenocrysts.	Almost unaltered; secondary Chl on Amph	N: 37.39925 E: 47.58888					

MN31	Andesitoid/Basaltoid (Diorite to monzo diorite porphyry)	Porphyritic with microgranular groundmass. Pl (30-35 %), Cpx (15-20 %) phenocrysts. Groudnmass: Pl (25-30 %), Cpx (15-20 %)+ Mag (4-6 %),	Propylitic alteration. Ep (10-15 %)+ Act/Tr (5-10 %), Py	N: 37.38710 E: 47.60161
MN65	Andesitoid/Basaltoid (monzodiorite)	Porphyritic with microgranular groundmass. Pl (20-30 %), Cpx (7-10 %), Opx (5 %) phenocrysts. Groundmass: Pl+KFs+Px+Mag (40-50 %)	Weakly propylitic alteration. Cb (disseminated over mafic minerals and Pl) and Cb veining (2-3 %), secondary Chl on Cpx and Opx.	N: 37.406533 E: 47.589648
MN55	Andesitoid/Basaltoid (monzonite porphyry)	Porphyritic with microgranular groundmass. Pl (5-7 %) phenocrysts. Groudnmass: Pl (60-70), KFs (5-10? %), Mag (5-7 %).	Weakly altered to Cb	N: 37.40281 E: 47.59006

1545 **15.**

1547   Table 2. Trace element chemistry of quartz from V2 veins

Spot	Li	B	Al	Mn	Ga	Ge	As
				ppm			
v4q	3.26	3.90	35.97	0.15	0.10	0.89	0.01
v4a2	24.52	5.18	156.97	1.05	0.11	1.41	2.02
v4b2	3.34	3.57	98.49	0.70	0.13	1.20	1.77
v4c2	6.50	8.35	89.96	0.27	0.01	1.98	0.94
v4d2	28.03	7.63	160.22	0.20	0.06	1.87	0.80
v4e2	1.86	4.58	45.10	0.24	bdl	bdl	0.14
v4f2	17.07	4.00	102.47	0.66	0.17	1.33	bdl

bdl: Below detection limit

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1551 Table 3. Ti-in-Quartz content and results of TitaniQ thermometry (V2 veins)

Spot	Ti (ppm)	Temperature (°C) calculated for P (kbar)				
		0.5	1	1.5	2	2.5
v4b	21.17	494	527	550	569	585
v4c	21.52	495	528	551	570	586
v4d	31.88	527	561	585	605	621
v4e	29.78	521	555	579	599	615
v4f	17.42	479	511	534	553	568
v4g	44.20	555	591	616	636	653
v4i	45.00	557	592	618	638	655
v4j	20.91	493	526	549	568	583
v4n	44.69	556	592	617	637	654
v4q	17.36	479	511	534	552	568
v4a2	54.65	575	611	637	657	675
v4b2	41.66	550	585	610	630	647

v 4c2	24.57	5 05	5 39	5 63	5 81	5 98
v 4d2	48.02	5 63	5 98	6 24	6 44	6 61
v 4e2	23.61	5 02	5 36	5 59	5 78	5 94
v 4f2	24.67	5 06	5 39	5 63	5 82	5 98

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1554 Table 4. Summary of the FI characteristics and the obtained microthermometry results

Type	V to L ratio	Host mineral	Alteration zone	Measured number	T freezing (°C)	T eutectic (°C)	T homogenization (°C)	T melting (°C)	Salinity (wt.% NaCl eq.)
Type A1 (L-rich+ V)	0.5-1	Quartz	Potassic	44	-44.4 to -29.6 (Mean= -38.5)	-30 to -22.5 (Mean= -25.3)	298 to 365 (Mean= 333)	-4,3 to -0,6 (Mean= -2)	1 to 6,9 (Mode= 3.85)
Type A2 (L-rich+ V)	0.1-0.4	Quartz	Potassic	195	-47.2 to -25.3 (Mean= -39)	-31.5 to -23 (Mode= -23)	170 to 352 (Mean= 272)	-3.7 to -0.1 (Mean= -1.5)	0.2 to 6 (Mean= 2.6)
Type A3 (L-rich+ V)	0.2-0.4	Quartz	Phyllic	52	-41.4 to -31 (Mean= -33.6)	-22 to -21 (Mean= -21.5)	232 to 365 (Mode= 320)	-2,6 to -1 (Mean= -1.8)	1.7 to 4.3 (Mean= 3.1)
Type A4 (L-rich+ V)	0.1-.25	Paraspurrite	Potassic	91	-30 to -42 (Mean= -39)	-24 to -33 (Mean= -27)	145 to 300 (Mode= 225)	-1,2 to -0,1 (Mean= -0.35)	0.2 to 2.1 (Mean= 0.6)

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| Type B (L-rich+ V±S) | 0.1-0.2 | Quartz | Potassic | 4 | -80 to -39.8 | -25 to -65 (Mean= -28.5 and -61) | 203 to 320 | -34 to -11.5 | 30.5 to 32 |

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1557　Table 5. Results of LA–ICP–MS U-(Th)-Pb zircon data.

MN01; Northing: 37.41297, Easting: 47.59745

MN03; Northing: 37.39916, Easting: 47.59519

MN19; Northing: 37.39925, Easting: 47.58888

MN31; Northing: 37.38710, Easting: 47.60161

1558 * 206 Percentage of Pb contributed by common Pb on the basis of 204 Pb. Value of common Pb was assumed by Stacey and Kramers (1975) model; n.d.: no detection of 204Pb

1559 ** Degree of discordance (%); negative numbers and blanks show normal discordant and concordant within 2σ of the analytical error, respectively.

1561 Table 6. Re-Os isotopic data for two molybdenite samples from the Siah-Kamar Mo deposit

Sample	wt (g)	Re (ppm)	:	^{187}Re (ppm)	:	^{187}Os (ppb)	:	Age	*	#
RO780-13_Mo1B	0.016	19.33	.09	12.15	.05	5.81	.02	28.70	.14	.17
RO780-14_Mo2B	0.016	22.14	.10	13.92	.06	6.56	.03	28.29	.14	.16

1562 *uncertainty including all sources of analytical uncertainty

1563 #uncertainty including all sources of analytical uncertainty plus decay constant

1565 Table 7. Rb-Sr analytical data for the mineral separated from sample MN02

Analysis	material	Rb ppm	Sr ppm	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$ $2\sigma_m$ (%)
PS3 104	biotite	306	194	4.56	0.707085	0.0019
PS3 105	kfsp >160 µm	138	875	0.455	0.705176	0.0011
PS3 106	sericite >125 µm	397	118	9.732	0.708913	0.0015
PS3 107	kfsp <160 µm	145	893	0.471	0.705179	0.0008
PS3 108	sericite <125 µm	375	190	5.72	0.707161	0.0022
PS3 109	apatite conc.	91.2	652	0.405	0.705162	0.0021

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Minerals	Style (Major/Minor)	Stage-1(V1) Na alteration / K alteration	Stage-2a (V2a) Phyllic-Silicic	Stage-2b (V2b) Siliceous-carbonatization	Stage-2b (V2b) Molybdenite enrichment and carbonatization
Magnetite	Minor (Brecciated)				
Albite	Major (Brecciated) / Minor (Veining)				
K-Feldspar I	Major (Brecciated) / Minor (Veining)				
Biotite	Major (Brecciated) / Minor (Veining)				
Ilmenite	Minor (Brecciated)				
Quartz I	Minor (Veining/Brecciated)				
Pyrrhotite	Minor (Veining)				
Molybdenite I	Minor (Disseminated)				
Apatite	Minor (Veining/Brecciated)				
K-Feldspar II	Major (Veining)				
Quartz II	Major (Brecciated/Veining)				
Anhydrite	Minor (Veining)				
Scheelite	Minor (Veining)				
Rutile	Minor (Veining)				
Molybdenite II	Minor (Brecciated/Veining)				
Pyrite	Major (Brecciated) / Minor (Veining)				
Quartz III	Major (Veining/Brecciated)				
Sericite	Major (Brecciated) / Minor (Veining)				
Paraspurite	Minor (Veining)				
Ankerite	Major (Veining)				
Rhodochrosite	Major (Veining)				
Calcite	Major (Veining)				
Molybdenite III	Major (Veining)				
Hemimorphite	Minor (Veining)				
Kaolinite	Minor (Veining)				

Mineralization styles
⁂ Disseminated
✕ Veining
❋ Brecciated

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1596 **Highlights**

1597   - Long-lived magmatism and differentiation control Mo ore mineralisation

1598   - Mo ore-enhancement caused by renewed magmatism

1599   - Mo ore associated with carbonatisation, acidic fluid neutralisation and

1600   cooling

1601   - Refertilised crust leading to Mo ore formation in the Urumieh-Dokhtar zone

1602