



HAL
open science

Remarkably uniform oxygen isotope systematics for co-existing pairs of gem-spinel and calcite in marble, with special reference to Vietnamese deposits

Anthony E. Fallick, Gaston Giuliani, Thomas Rigaudier, Adrian J. Boyce, van Long Pham, Vincent Pardieu

► To cite this version:

Anthony E. Fallick, Gaston Giuliani, Thomas Rigaudier, Adrian J. Boyce, van Long Pham, et al.. Remarkably uniform oxygen isotope systematics for co-existing pairs of gem-spinel and calcite in marble, with special reference to Vietnamese deposits. *Comptes Rendus. Géoscience*, 2019, 351, pp.27 - 36. 10.1016/j.crte.2018.11.008 . hal-03485971

HAL Id: hal-03485971

<https://hal.science/hal-03485971>

Submitted on 20 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **Remarkably uniform oxygen isotope systematics for co-existing pairs of gem-spinel and**
2 **calcite in marble, with special reference to Vietnam deposits**

3
4
5 Anthony E. Fallick¹, Gaston Giuliani^{2,3}, Thomas Rigaudier³, Adrian J. Boyce¹, Van Long Pham⁴, Vincent
6 Pardieu⁵

7
8 1- Isotope Geosciences Unit, S.U.E.R.C., Rankine Avenue, East Kilbride, Glasgow G75 0QF, Scotland, United
9 Kingdom

10 Anthony.Fallick@glasgow.ac.uk

11 Adrian.Boyce@glasgow.ac.uk

12
13 2- Université Paul Sabatier, GET/IRD, UMR CNRS-IRD-CNRS 5563, 14 avenue Edouard Belin, 31400
14 Toulouse, France

15 giuliani@crpg.cnrs-nancy.fr

16
17 3- Université de Lorraine, CRPG UMR 7358 CNRS-UL, 15 rue Notre-Dame-des-Pauvres, BP 20, 54501
18 Vandœuvre-lès-Nancy cedex, France

19 trigaud@crpg.cnrs-nancy.fr

20
21 4- Centre for Gems and Gold Research and Identification of Vietnam, 91 Dinh Tien Hoang Hanoi, Vietnam
22 long@vinagems.vn

23
24 5- Field gemmologist, Bangkok, Thailand

25 vince@fieldgemmology.org

26
27
28
29
30 Corresponding author:

31 Giuliani Gaston

32 CRPG/CNRS

33 15 rue Notre-Dame-des-Pauvres,

34 BP 20,

35 54501 Vandœuvre-lès-Nancy cedex, France

36
37 giuliani@crpg.cnrs-nancy.fr

38 (33) 3 83 59 42 38

39 (33) 3 83 51 17 98

59 **Abstract** Oxygen isotope systematics for co-existing pairs of gem-spinel and calcite in
60 marble from Vietnam and other worldwide deposits have been determined in order to
61 characterize the O-isotope fractionation between calcite and spinel. In Vietnam, the $\Delta^{18}\text{O}_{\text{cc-sp}}$
62 = $3.7 \pm 0.1\text{‰}$ for six samples from the An Phu and Cong Troi deposits is remarkably constant.
63 The combination of these data with those obtained on calcite-spinel pairs of Paigutan (Nepal,
64 n = 2), Ipanko (Tanzania, n= 1) and Mogok (Myanmar, =2) are also consistent, overall $\Delta^{18}\text{O}_{\text{cc-}}$
65 sp of $3.6 \pm 0.25\text{‰}$ for all the spinel samples (n=11) with an excellent straight line correlation:
66 $\delta^{18}\text{O}_{\text{cc}} = 0.96\delta^{18}\text{O}_{\text{sp}} + 4.4$, despite their worldwide geographic spread. The increment method
67 of calculating oxygen isotope fractionation gave a geologically unreasonable temperature of
68 formation for both minerals at 1374°C when compared to temperatures obtained by mineral
69 assemblage equilibrium of these marble type deposits, between 610 and 750°C . The constant
70 $\Delta^{18}\text{O}_{\text{cc-sp}}$ reflects a constant temperature for this amphibolite facies assemblage, whose current
71 best estimates is calculated at $620 \pm 40^\circ\text{C}$ but unquantified uncertainties remain.

72

73 **Keywords** marble deposits, Asia, East Africa, spinel-calcite pair, oxygen isotope
74 fractionation, temperature of formation

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

92 **Introduction**

93

94 There is much current interest in using geochemical and isotopic techniques to decipher and
95 discriminate the geologic and/or geographic origin of gemstones (see e.g. Giuliani et al., 2014
96 and references therein) and such work both informs, and is informed by, genetic ideas about
97 gemstone formation. For example, in the case of red and pink spinels found in marbles
98 worldwide, Giuliani et al. (2017) recently published a trace element and oxygen stable isotope
99 ratio database that permits useful characterization of the main currently productive and
100 historical sources of gem spinel. The study included samples from classic sites of Mogok in
101 Myanmar, and Kuh-i-Lal in Tajikistan, as well as material from Vietnam, Nepal, Pakistan,
102 Tanzania and Kenya.

103 At the local level, given the metamorphic origin of many of the spinels, the utility of $\delta^{18}\text{O}$
104 decreases because the parental fluid of the minerals can be isotopically buffered by the host
105 impure marble, and many marine carbonates and their marble counterparts have (in the
106 absence of metasomatic alteration) a rather restricted range of depositional $\delta^{18}\text{O}$ through
107 geological time (see e.g. discussion in Veizer, 1992). Thus, in the specific case of spinels of a
108 wide palette of colours from Vietnam, Pham et al. (2018) have pointed out that whilst there is
109 a considerable range in spinel $\delta^{18}\text{O}$ (spanning 12.1 to 24.2‰ for 32 specimens),
110 discrimination amongst geographically distinct deposits is not possible using oxygen isotopes
111 alone, whereas it can be accomplished using selected trace elements (specifically Fe-Zn-Cr-
112 V) whose concentrations are presumably locally controlled by the impure nature of the host
113 marbles.

114 These considerations offer an opportunity to look a little more closely into the genetic model
115 for the Vietnamese spinels, to investigate in greater detail the factors influencing their $\delta^{18}\text{O}$
116 values and to enquire whether any conclusions reached might have more widespread utility
117 and applications to metallogenesis. Within this overall framework, the present study will
118 encompass the oxygen isotope composition of calcite-spinel pairs of Vietnamese and other
119 worldwide deposits in order to characterize the O-isotope fractionation between calcite and
120 spinel and to estimate the temperature of formation for spinel. Discrepancies between the
121 calculated temperatures by incremental method for oxygen isotope fractionation and those
122 derived by phase diagram considerations are discussed as well as the use of oxygen isotopes
123 for deciphering the geographic origin of spinels.

124

125 **Geological background of gem spinel deposits in marble with a special focus on**
126 **Vietnamese mineralization**

127

128 Gem spinels in marble have compositions close to $MgAl_2O_4$ *sensu stricto* and the most
129 appreciated are the pink, orange or red crystals (Fig. 1). World-economic Cr-V-bearing
130 spinels occur in Himalayan and East Africa and formed under high-degree metamorphic
131 conditions in the amphibolite facies (Giuliani et al., 2017).

132 In Asia, the main primary deposits (Fig. 2) are located in marble intercalated within the high-
133 grade metamorphic gneisses of the Lo Gam zone in northern Vietnam (Giuliani et al., 2017),
134 Myanmar in the Mogok Metamorphic Belt exposed along the meridian trending Shan scarp
135 and Sagain fault (Searle et al., 2007), Tajikistan in the metamorphic series of the southwest
136 Pamirs (Kievlenko, 2003), and minor occurrences in Pakistan at the Hunza valley (Okrush et
137 al., 1976) and Nepal in the Navakot series of the Ganesh Himal (Garnier et al., 2006).

138 In East Africa, the spinel deposits are located in the Neoproterozoic Metamorphic
139 Mozambique Belt and formed during the East African Orogeny (Giuliani et al., 2017). Gem
140 spinels are related to marble at Pamreso in Kenya, in the Voi area, and in Tanzania, in the
141 Mahenge and Uluguru mountains, respectively at Ipanko and Morogoro deposits (Balmer et
142 al., 2017; Giuliani et al., 2017).

143

144 Gem quality Vietnamese spinels have been mined since 1987 in the Luc Yen and An Phu
145 mining districts (Yen Bai Province, Fig. 3). The primary deposits are linked with the
146 formation of the sinistral Red River Shear Zone, during the Tertiary, when the north-moving
147 Indian plate collided with the Eurasian plate to form the Himalayan mountain belt, with
148 Indochina extruded to the SE (Tapponnier et al., 1990; Leloup et al., 1995). Amphibolite
149 facies metasedimentary sequences of Cambrian depositional age, formed of marble units and
150 intercalated gneisses and schists, are situated in the Lo Gam Zone (Fig. 3), between two left-
151 lateral faults of the mainly 10-15 km wide Red River Shear Zone, and with intrusions of
152 granitoids of Triassic age (Garnier, 2003). The spinel deposits extend between Luc Yen and
153 An Phu localities either in marbles or placers (Fig. 3). The Luc Yen mining district
154 encompasses principally the mines of Nuoc Ngap, Khoan Thong, Luc Yen and Minh Thien
155 and the An Phu mining district including the well-known Cong Troi deposit. Spinel in
156 primary deposits occurs either as crystals disseminated in marbles or associated mostly with
157 calcite, dolomite, forsterite, clinohumite, pargasite-edenite, phlogopite and clinochlore.

158

159 **Material and methods**

160

161 Spinel from Vietnam primary and secondary deposits were sampled, between 1998 and
162 2013, in the field by Giuliani, Pardieu and Pham. Oxygen isotopes analyses (n = 32) were
163 performed at S.U.E.R.C. Glasgow (Scotland) using a modification of the laser -fluorination
164 technique (see Giuliani et al., 2005). Data are reported in the conventional $\delta^{18}\text{O}$ notation as
165 per mil (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW). The oxygen
166 isotope database of spinel worldwide published by Giuliani et al. (2017) and Pham et al.
167 (2018) is presented in a modified version in ESM Table 1.

168 Calcite and spinel pairs have been chosen after close examination by microscopy of the
169 mineral assemblages. It concerns mineral pairs originating from the deposits of An Phu (n =
170 3) and Cong Troi (n = 3) in Vietnam, Paigutan (n = 2) in Nepal, Ipanko (n = 1) in Tanzania,
171 and Mogok in Myanmar (n = 2 from Yui et al. 2008).

172 Carbon and oxygen isotopic compositions of calcite were determined by using an auto
173 sampler Gasbench coupled to a Thermo Scientific MAT253 isotope ratio mass spectrometer
174 (IRMS) at the CRPG UMR 7358 CNRS-UL, Vandœuvre-lès-Nancy (France). For each
175 sample, an aliquot between 250 to 300 μg of carbonate was reacted with 2 mL of
176 supersaturated orthophosphoric acid at 70 °C for at least 5 hours under a He atmosphere.
177 Carbon and oxygen isotopic compositions of the produced CO_2 were then measured with a
178 Thermo Scientific MAT 253 continuous flow isotope ratio mass spectrometer. Values are
179 quoted in the delta notation in ‰ relative to V-PeeDeeBelemnite (V-PDB) for carbon and to
180 V-SMOW for oxygen. All sample measurements were adjusted to the internal reference
181 calibrated on the international standards IAEA CO-1, IAEA CO-8 and NBS 19. Stable isotope
182 compositions of calcite and spinel are presented in Table 1. The O-isotope fractionation
183 between calcite and spinel is expressed such as $\Delta^{18}\text{O}_{\text{cc-sp}}$.

184

185 **Vietnamese spinel $\delta^{18}\text{O}$**

186

187 The oxygen isotope database for the current discussion comprises the 32 analyses previously
188 documented (Giuliani et al., 2017; Pham et al., 2018). The specimens came from three
189 localities An Phu, Cong Troi and Bai Son separated from each other by a few kilometres;
190 primary, placer and alluvium occurrences are represented (see SM Table 1). A very wide
191 range of colours are exhibited and the mineral parageneses are varied. Previously,

192 Hauzenberger et al. (2003) reported a single $\delta^{18}\text{O}$ of 14.3‰ for a purple spinel from Luc Yen,
193 also in the Lo Gam Zone, but cautioned that the silicate minerals in the sample were not in
194 oxygen isotope equilibrium. Figure 4 plots the 32 spinel $\delta^{18}\text{O}$ (‰, V-SMOW) data as a quasi-
195 histogram with datapoints identified by host deposit and spinel colour range. It is readily
196 apparent that two narrow intervals (approximately 14.2 to 14.9‰ and 22.4 to 22.9‰)
197 spanning only one tenth of the total range contain almost half (15 out of 32) of the samples,
198 with the remainder being spread with low frequency over the rest of the entire range (of 12 to
199 24‰). The value of 14.3‰ from Hauzenberger et al. (2003) falls in the first interval. Each of
200 the observed $\delta^{18}\text{O}$ modes (at ~14 and ~22‰) contains specimens from at least two
201 occurrences and with a wide range of colours indicating a rather wide range of trace element
202 concentrations (Pham et al., 2018), and each includes at least one primary deposit.

203 These observations reasonably preclude an explanation of the data distribution as being an
204 artifact of very close sampling of spatially restricted but spinel-rich areas of the marble hosts.
205 Rather, it seems more likely that there is a range in $\delta^{18}\text{O}$ of host marbles for all three
206 occurrences, and that locally two marble zones differing in $\delta^{18}\text{O}$ by ~8‰ are especially
207 productive. Mixing (e.g. near marble zone boundaries), Rayleigh decarbonation isotope
208 effects and perhaps even metasomatism (as discussed in Hauzenberger et al. (2003) for their
209 spinel-bearing sample) might all also be locally influential in affecting marble and so spinel,
210 $\delta^{18}\text{O}$.

211 This discussion helps to elucidate why spinel $\delta^{18}\text{O}$ is not geographically diagnostic for these
212 Vietnamese deposits, as has been previously pointed out by Pham et al. (2018). At each
213 occurrence there are the same two influential marbles with different oxygen isotopic
214 compositions. Additionally, it may be of economic exploration interest that spinels from the
215 high (~22‰) $\delta^{18}\text{O}$ mode have all been recovered from placers: the primary deposit has not
216 been sampled for the spinels discussed here.

217

218 **Further considerations and O-data of calcite associated with spinel**

219

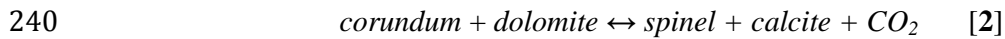
220 An intriguing feature of the data distribution, illustrated in Figure 4 is how narrow the two
221 modes are: for the lower $14.2 \pm 0.2\text{‰}$ (1σ , $n=8$) and for the higher $22.7 \pm 0.2\text{‰}$ (1σ , $n=7$).
222 The analytical precision of the laser fluorination method for determining $\delta^{18}\text{O}$ of high-Mg
223 minerals is likely 0.1 to 0.2‰ at 1σ , indicating very little geological scatter in the data from
224 the two or three occurrences within each mode. A metamorphic spinel (s) precipitating in

225 oxygen isotopic equilibrium from a fluid (f) at temperature T (°K) will have an oxygen
226 isotopic composition which can be represented by a polynomial in 1/T and frequently, to
227 reasonable approximation (O'Neil, 1986), expressed as:

$$228 \quad \delta^{18}\text{O}_s - \delta^{18}\text{O}_f = A_{sp}T^{-2} + B_{sp} \quad [1]$$

229 where A_{sp} , B_{sp} are mineral-specific numerical constants (which, to our knowledge, have not
230 been empirically evaluated for spinel). If for a suite of spinels $\delta^{18}\text{O}_f$ is buffered by the host
231 marble and is uniform, then a constant $\delta^{18}\text{O}_{sp}$ implies a constant spinel precipitation
232 temperature, and this argument applies equally to any other mineral co-crystallized with the
233 spinel (and in oxygen isotopic equilibrium with it), which does not subsequently exchange
234 oxygen isotopes.

235 Spinel in marble are markers of the high temperature metamorphism that affected the
236 marbles (Okrusch et al., 1976; Hauzenberger et al., 2001; Garnier et al., 2008). In the
237 amphibolite facies conditions, spinel, sapphirine and corundum are the main stable mineral
238 phases and the main equilibrium reaction between corundum and spinel during prograde
239 metamorphism is the following:



241 and then calcite coexisting (ideally in textural equilibrium) with spinel is of especial interest
242 since combining by subtraction [1] with the equivalent equation for calcite (cc) readily gives:

$$243 \quad \delta^{18}\text{O}_{cc} - \delta^{18}\text{O}_{sp} = \Delta^{18}\text{O}_{cc-sp} = (A_{cc} - A_{sp})T^{-2} + (B_{cc} - B_{sp}) \quad [3]$$

244 so that at constant T the oxygen isotopic difference between the calcite and spinel should be a
245 constant.

246 In a study of stable isotope ratios of Mogok ruby from Myanmar, Yui et al. (2008) reported
247 two spinel $\delta^{18}\text{O}$ values of $22.2 \pm 0.1\text{‰}$ (n=2) and $19.7 \pm 0.0\text{‰}$ (n=2) associated with closely
248 adjacent calcites of respective $\delta^{18}\text{O}$ of 25.3‰ and 23.7‰, giving $\Delta^{18}\text{O}_{cc-sp}$ of 3.1 and 4.0‰.
249 They noted that geologically unreasonable (because too high, approaching 1000°C)
250 equilibrium temperatures were deduced if the isotope fractionation equations (essentially the
251 A and B values) theoretically calculated by Zheng (1991) by the increment method were
252 adopted. The “isotopic inheritance” mechanism of Zheng (2011) was discussed but
253 discounted.

254

255 The calcite-spinel mineral pair approach was largely restricted to carefully examined primary
256 specimens and six such samples were identified from the seven primary specimens from An
257 Phu and Cong Troi deposits, and calcite $\delta^{18}\text{O}$ was measured. The data are given in **Table 1**

258 and the $\Delta^{18}\text{O}_{\text{cc-sp}}$ values range from 3.5 to 3.9 (mean $3.73 \pm 0.15\text{‰}$, $n=3$ for An Phu, and 3.67
259 $\pm 0.15\text{‰}$, $n=3$ for Cong Troi) with overall mean $3.7 \pm 0.1\text{‰}$, $n=6$. For the samples from
260 Vietnam, therefore, there certainly appears to be a very consistent relationship of constant
261 $\Delta^{18}\text{O}_{\text{cc-sp}}$ independent of the actual $\delta^{18}\text{O}_{\text{sp}}$ value. This conclusion raises the question of whether
262 the observed relationship might be of more than local significance: certainly $\delta^{18}\text{O}_{\text{cc-sp}} \sim 3.7\text{‰}$
263 for Vietnam is remarkably similar to the Yui et al. (2008) values of 3.1 and 4.0‰ from
264 Myanmar, suggesting at least a regional character.

265 Accordingly, additional appropriate calcite-spinel mineral pairs were sought for primary
266 deposit specimens from amongst the worldwide database reported by Giuliani et al. (2017)
267 and suitable material was available from Tanzania (sample IPAN2) and Nepal (samples G85-
268 1 and G85-2). The data for these, together with the Myanmar data of Yui et al. (2008) are
269 included in Table 1. The $\delta^{18}\text{O}$ data for the two Nepal samples are analytically
270 indistinguishable and give $\Delta^{18}\text{O}_{\text{cc-sp}}$ of 3.6 and 3.3‰, whilst for IPAN 2 from Tanzania the
271 value is 3.4‰. We note that Hauzenberger et al. (2003) reported spinel $\delta^{18}\text{O}$ of 14.3‰ from
272 Luc Yen in Vietnam, but only present a range of host rock (not necessarily equilibrium
273 assemblage) calcite $\delta^{18}\text{O}$ values (25.65 to 26.16‰) and, as noted previously, claimed that the
274 various silicate minerals present were “...not in equilibrium”. Therefore, we have not
275 included these data in the current analysis.

276 For the 9 pairs of new data reported in this study, the $\Delta^{18}\text{O}_{\text{cc-sp}}$ values range from 3.3 to 3.9‰
277 with mean $3.6 \pm 0.18\text{‰}$ ($n=9$). Including the Myanmar data from Yui et al. (2008) expands
278 the range slightly 3.1 to 4.0‰ with overall mean $3.6 \pm 0.3\text{‰}$ (1σ , $n=11$). $\delta^{18}\text{O}_{\text{cc}}$ is plotted
279 against $\delta^{18}\text{O}_{\text{sp}}$ in **Figure 5** and the best-fit line for all 11 samples is $\delta^{18}\text{O}_{\text{cc}} = 0.96 \delta^{18}\text{O}_{\text{sp}} + 4.4$,
280 with $r = 0.9974$ which is significant above the 99.9% level for $n=11$. Clearly, there is very
281 little geological ‘noise’ in the spinel-calcite $\delta^{18}\text{O}$ relationship despite their worldwide
282 geographical spread and almost 10‰ range in $\delta^{18}\text{O}$.

283

284 **Discussion**

285

286 We are not aware of any empirical calibration of equilibrium oxygen isotope partitioning
287 between spinel and another mineral phase as a function of temperature. Accordingly we first
288 investigated the efficacy of the increment-method theoretical approach of Zheng (1991), and
289 for the calcite-spinel pair calculated 1647 °K ($T = 1374$ °C) for $\Delta_{\text{cc-sp}}$ of 3.6‰, and so concur
290 with Yui et al. (2008) that this approach generates temperatures too high to be geologically

291 reasonable. Zheng (1995) has claimed that for magnetite different structural forms have
292 different oxygen isotope partitioning behaviour, and that this can on occasion lead to an
293 oxygen isotope composition inherited from a precursor phase of different structure. However,
294 we further concur with Yui et al. (2008) that such a mechanism does not seem likely in the
295 case of the spinels discussed here.

296 The situation is not improved by using only the spinel-water calibration of Zheng (1991)
297 together with an empirical calcite-water calibration: adopting the classic (O'Neil et al. 1969;
298 and see also Kim and O'Neil, 1997) calcite-water equation gives a similarly unreasonable
299 temperature of over 1000°C. It would seem that the problem lies with the increment-method
300 approach to spinel. As an alternative, we use the observation of a relatively constant oxygen
301 isotope fractionation between clinopyroxene (cpx) and spinel in high temperature mineral
302 assemblages. Of course, the magnitude of such fractionation is temperature sensitive, but the
303 error introduced is likely small, of the order of a few tenths of one per mil for the
304 temperatures of interest. For the Vitim xenolith suite in southern Siberia, argued to reflect the
305 bulk O-isotope character of the Earth's upper mantle (at $5.6 \pm 0.1\%$), Ionov et al. (1994)
306 reported $\Delta^{18}\text{O}_{\text{cpx-sp}}$ of $0.6 \pm 0.35\%$ where the analytical precision was stated to be "...ca. ± 0.2
307 $- 0.3\%$ ". They noted that the spinel peridotite xenoliths from Mongolia (Harmon et al., 1987)
308 had similar overall oxygen isotope characteristics to those at Vitim, albeit no spinel data were
309 reported, presumably because of the low abundance of spinel at this location.

310 Then since $\Delta_{\text{cpx-cc}} = \Delta_{\text{cpx-sp}} - \Delta_{\text{cc-sp}}$ and from the empirical calibration of Chiba et al. (1989) for
311 the pyroxene group mineral diopside:

$$312 \Delta_{\text{cpx-cc}} = 10^3 \ln \alpha_{\text{diopside(or sp)-calcite}}^{18} = -2.37 \cdot 10^6 / T^2$$

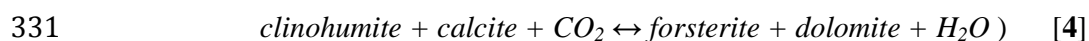
313 we obtain by substitution for the average $\Delta^{18}\text{O}_{\text{cc-sp}}$ of 3.6 ± 0.25 (n=11) and adding the $\Delta^{18}\text{O}_{\text{cpx-}}$
314 sp of 0.6 reported by Ionov et al. (1994), respectively $-2.37 \cdot 10^6 / T^2 = 0.6 - 3.6$ or $T = 889 \text{ K}$ (T
315 $= 616^\circ\text{C}$).

316 Propagating the $\pm 0.25\%$ standard deviation of the mean $\Delta^{18}\text{O}_{\text{cc-sp}} = 3.6\%$ generates a
317 minimum uncertainty of approximately $\pm 40^\circ\text{C}$.

318 This temperature estimate of $616 \pm 40^\circ\text{C}$ seems geologically more plausible than the earlier
319 estimates based on the increment-method oxygen isotope fractionation factor for spinel-water.
320 Because of unquantified imprecision and inaccuracy in the overall approach adopted here, the
321 main point is not to derive a robust temperature estimate together with an assessment of the
322 associated error, but rather to suggest that equilibrium oxygen isotope fractionation at a

323 constant and geologically reasonable temperature can explain the remarkably consistent
324 difference in $\delta^{18}\text{O}$ between calcite and spinel on local and global scales.

325 General estimates of pressure-temperature (P-T) conditions of peak metamorphism for the
326 Day Nui Con Voi Range (Fig. 3) are constrained by biotite-garnet-sillimanite paragneisses at
327 7 kbar and 780°C (Leloup et al., 1995). In the Lo Gam Zone where are located the ruby and
328 spinel deposits in marble, these P-T conditions correspond to the presence of the mineral
329 assemblage clinohumite - calcite - forsterite - dolomite - spinel (Hauzenberger et al., 2014)
330 following the reaction:



332 and spinel formed during the prograde path at a minimum T of 700 °C.

333 Garnier et al. (2008) using mineral assemblages and fluid inclusions data in ruby deposits
334 from south-east Asia, suggested the formation of ruby during the prograde and retrograde
335 paths in the range $610 < T < 670^\circ\text{C}$ and $3 < P < 6$ kbar. Ruby is found sometimes with spinel
336 but generally spinel formed by the disappearance of ruby following reaction [2] and in the
337 absence of sapphirine. The estimate metamorphic P-T conditions for spinel formation are $3 <$
338 $P < 6.5$ kbar and $610 < T < 750^\circ\text{C}$ (Fig. 6). Yui et al. (2008) estimated temperatures of 607
339 and $< 710^\circ\text{C}$ as upper limits for spinel and ruby at Mogok in Myanmar, based on Raman
340 spectra of graphite, with the higher of these temperatures being for a spinel-bearing
341 assemblage.

342 During subsequent cooling, any free fluid phase would have its oxygen isotopic composition
343 buffered by the relatively great volume of host marble, and so we do not expect any oxygen
344 isotope closure issue (as in Jenkin et al., 1991) to affect measured calcite $\delta^{18}\text{O}$.

345

346 The $\delta^{18}\text{O}$ values of Vietnamese spinels (An Phu and Luc Yen area) defined two narrow
347 intervals, respectively 14.2 to 14.9‰ and 22.4 to 22.9‰ (Fig. 4) and the calcite-spinel pairs
348 have a remarkably constant $\Delta^{18}\text{O}_{\text{cc-sp}}$ of 3.7 ± 0.1 (n = 6). The excellent correlation with other
349 worldwide cc-sp pairs ($\Delta^{18}\text{O}_{\text{cc-sp}}$ of 3.6 ± 0.25 , n= 11 ; Fig. 5) signifies that the oxygen isotope
350 fractionation factor is applicable to all calcite and spinel association which grew in
351 equilibrium during metamorphism. Garnier (2003) have shown that in the Luc Yen and An
352 Phu mining districts, the O-isotopic composition of calcite and dolomite in marbles vary from
353 one district to another, but were homogeneous in each districts. The $\delta^{18}\text{O}$ values of these
354 carbonates, between 18 and 29‰ (n = 22 ; Table SM 2), define two ranges, respectively 18 to
355 21.5‰ and 24 to 28.9‰ (Fig. 7) The first $\delta^{18}\text{O}$ range of marble fits with the $\delta^{18}\text{O}$ values of

356 calcite in equilibrium with spinel (this study) corroborating the calculated $\Delta^{18}\text{O}_{\text{cc-sp}}$ of around
357 4.0. The existence of $\delta^{18}\text{O}$ values between 21 and 24‰ for spinels from placers of both An
358 Phu and Luc Yen open the question about the isotopic composition of calcite of the spinel-
359 bearing marble. Taking in account the $\Delta^{18}\text{O}_{\text{cc-sp}} \sim 4.0$, the $\delta^{18}\text{O}$ values of calcite from marble
360 must be within the range $\sim 24\text{-}25$ and 29‰. Figure 7 shows that such a range of $\delta^{18}\text{O}$ values is
361 found for both marbles from Luc Yen and An Phu mining districts. This result indicates that a
362 great part of the spinels found in placers originates from high- $\delta^{18}\text{O}$ carbonates mother rock
363 that could be a parameter used for geochemical prospecting of spinel occurrences in northern
364 Vietnam.

365

366 **Conclusions and perspectives**

367 The main conclusions of this study can be summarized as follow:

368 (1) For gem spinels associated with marbles from a variety of locations in Vietnam, there is a
369 remarkably constant oxygen isotope fractionation between the oxygen in the spinel oxide
370 structure and that in the carbonate of genetically-associated calcite with $\Delta^{18}\text{O}_{\text{cc-sp}} = 3.7 \pm 0.1\text{‰}$
371 (n=6).

372 (2) A similar relationship has been observed for material from Myanmar, with values of 3.1
373 and 4.0‰ (Yui et al., 2008). New data reported here from Nepal (3.1 and 3.3‰) and Tanzania
374 (3.4‰) are also consistent, overall $\Delta^{18}\text{O}_{\text{cc-sp}}$ of $3.6 \pm 0.25\text{‰}$ for all the spinel samples (n=11).
375 We hypothesise that the observed relationship has a global character. There is no evidence of
376 any strong influence of other parameters (such as pressure or fluid salinity).

377 (3) Whilst the equilibrium temperature implied by the increment method of calculating
378 oxygen isotope fractionation (Zheng, 1991) is at 1374°C geologically unreasonable, a more
379 indirect assessment of the temperature dependence of the oxygen isotope partitioning in
380 systems involving spinel suggests that the constant oxygen isotope fractionation observed
381 between coexisting spinel and calcite reflects a constant temperature, whose current best
382 estimate is $\sim 620 \pm 40\text{°C}$, but unquantified uncertainties associated with various steps in the
383 argument preclude robust estimate of the accuracy of this estimation.

384 (4) These observations buttress the emerging genetic model (Giuliani et al., 2017) for
385 economically gem spinels, including an explanation of why spinel $\delta^{18}\text{O}$ is not, on its own,
386 locally a discriminant of geographic origin (Pham et al., 2018), and offer a critical diagnostic
387 test (different $\Delta^{18}\text{O}_{\text{cc-sp}}$) for deposits (likely restricted to primary examples) which conform to
388 any different genetic model.

389 **Funding sources**

390 This research did not receive any specific grant from funding agencies in the public,
391 commercial, or not-profit sectors.

392

393 **References**

394

395 Balmer, W.A., Hauzenberger, C.A., Fritz, J., Sutthirat, C., 2017. Marble-hosted deposits of
396 the Morogoro region, Tanzania. *J. Afr. Earth Sci.* 134, 626-643.

397 Berman, R.G., 1991. Thermobarometry using equilibrium calculations: a new technique with
398 petrologic applications. *Can. Mineral.* 29, 833-855.

399 Chiba, H., Chacko, T., Clayton, R.N., Goldsmith, J.R., 1989. Oxygen isotope fractionations
400 involving diopside, forsterite, magnetite and calcite: Applications to geothermometry.
401 *Geochim. Cosmochim. Acta* 53, 2985-2995.

402 Garnier, V., 2003. Les gisements de rubis associés aux marbres de l'Asie Centrale et du Sud-
403 est: genèse et caractérisation isotopique. Ph.D. Thesis INPL, Nancy, France.

404 Garnier, V., Maluski, H., Giuliani, G., Ohnenstetter, D., Schwarz, D., 2006. Ar-Ar and U-Pb
405 ages of marble-hosted ruby deposits from central and southeast Asia. *Can. J. Earth Sci.*
406 43, 509-532.

407 Garnier, V., Giuliani, G., Ohnenstetter, D., Fallick, A.E., Dubessy, J., Banks, D., Vinh, H.Q.,
408 Lhomme, T., Maluski, H., Pêcher, A., Baksh, K.A., Pham, V.L., Trinh, P.T., Schwarz,
409 D., 2008. Marble-hosted ruby deposits from Central and Southeast Asia: Towards a new
410 genetic model. *Ore Geol. Rev.* 34, 169-191.

411 Giuliani, G., Fallick, A.E., Boyce, A.J., Pardieu, V., Pham, V.L., 2017. Pink and red spinels
412 in marble: trace elements, oxygen isotopes, and sources. *Can. Mineral.* 55, 743-761

413 Giuliani, G., Groat, L., Ohnenstetter, D., Fallick, A.E., Feneyrol, J., 2014. Geology of gems
414 and their geographic origin, in: Groat, L.A. (Ed.), *Geology of Gem Deposits 2nd edition*.
415 Mineralogical Association of Canada Short Course Series, volume 44, Tucson Arizona,
416 pp 113-134.

417 Giuliani, G., Fallick, A.E., Garnier, V., France-Lanord, Ch., Ohnenstetter, D., Schwarz, D.,
418 2005. Oxygen isotope composition as a tracer for the origins of rubies and sapphires.
419 *Geology* 33, 249-252.

420 Grew, E.S., Pertsev, N.N., Yates, M.G., Christy, A.G., Marquez, N., Chernosky, J.C., 1994.
421 Sapphirine + forsterite and sapphirine + humite-group minerals in an ultramagnesian

422 lens from Kuh-i-Lal, SW Pamirs, Tajikistan: are these assemblages forbidden? *J. Petrol.*
423 35, 1275-1293.

424 Harmon, R.S., Kempton, P.D., Stosch, H.G., Hoefs, J., Kovalenko, V.I., Ionov, D.A., 1986/7.
425 O-18/O-16 ratios in anhydrous spinel lherzolite xenoliths from the Shavaryn-Tsaram
426 Volcano, Mongolia. *Earth Planet. Sci. Lett.* 81, 193-202.

427 Hauzenberger, C.A., Häger, T., Baumgartner, L.P., Hofmeister, W., 2001, High-grade
428 metamorphism and stable isotope geochemistry of N-Vietnamese gem-bearing rocks,
429 in: *Proceedings of the Workshop on gems and minerals of Vietnam*, Hanoi, pp. 124-
430 138.

431 Hauzenberger, C.A., Häger, T., Hofmeister, W., Quang, V.X., Fernando, Q.W.A.R., 2003.
432 Origin and formation of gem quality corundum from Vietnam, in: *Proceedings of the*
433 *International Workshop, Geo- and Material-Science on Gem Minerals of Vietnam.*
434 Hanoi, pp 1-8.

435 Hauzenberger, C.A., Bagola, C., Haeger, T., Muellen, C., Khoi, N.N., Huong, L.T.T., 2014.
436 Mineralogy and petrology of the An Phu marble hosted spinel and corundum deposit,
437 Luc Yen, N-Vietnam, in: *Proceedings of the 4th International Gem and Jewelry*
438 *Conference*, Chiang Mai, pp 76-78.

439 Ionov, D.A., Harmon, R.S., France-Lanord, Ch., Greenwood, P., Ashchepkov, I.V., 1994.
440 Oxygen isotope composition of garnet and spinel peridotites in the continental mantle:
441 Evidence from the Vitim xenolith suite, southern Siberia. *Geochim. Cosmochim. Acta*
442 58, 1463-1470.

443 Jenkin, G.R.T., Linklater, C., Fallick, A.E., 1991. Modelling of mineral $\delta^{18}\text{O}$ values in an
444 igneous aureole: closed-system model predicts apparent open-system $\delta^{18}\text{O}$ values.
445 *Geology* 19, 1185-1188.

446 Kievlenko, E.Y., 2003. *Geology of Gems*. Ocean Pictures Ltd, Littleton, CO, USA.

447 Kim, S.T., O'Neil, J.R., 1997. Equilibrium and non-equilibrium oxygen isotope effects in
448 synthetic carbonates. *Geochim. Cosmochim. Acta* 61, 3461-3475.

449 Leloup, P.H., Lacassin, R., Tapponnier, P., Schärer, U., Zhong, D., Liu, X., Zhang, L., Ji, S.,
450 Trinh, P.T., 1995. The Ailao Shan-Red River shear zone (Yunnan, China), Tertiary
451 transform boundary of Indochina. *Tectonophysics* 251, 3-84.

452 Mattauer, M., Matte, Ph., Jolivet, J.L., 1999. A 3D model of the India-Asia collision at large
453 scale. *C. R. Acad. Sci. Paris* 328, 499-508.

454 Okrusch, M., Bunch, T.E., Bank, H., 1976. Paragenesis and petrogenesis of a corundum-
455 bearing marble at Hunza (Kashmir). *Mineral. Deposita* 11, 278-297.

456 O'Neil, J.R., 1986. Theoretical and experimental aspects of isotopic fractionation, in: Valley,
457 J.W., Taylor, H.P., O'Neil, J.R. (Eds), Stable isotopes in high temperature geological
458 processes. Reviews in Mineralogy and Geochemistry, 16, Chelsea, Michigan, , pp. 1-40.
459 O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent
460 metal carbonates. J. Chem. Phys. 51, 5547-5558.
461 Pham, V.L., Giuliani, G, Fallick, A.E., Boyce, A.J., Pardieu, V., 2018. Trace elements and
462 oxygen isotopes of gem spinels in marble from the Luc Yen - An Phu areas, Yen Bai
463 province, North Vietnam. Vietnam. J. Earth Sci. 40, 166-179.
464 Searle, M.P., Noble, S.R., Cottle, J.M., Waters, D.J., Mitchell, A.H.G., Hlaing, T.,
465 Horstwood, M.S.A., 2007. Tectonic evolution of the Mogok metamorphic belt, Burma
466 (Myanmar) constrained by U-Th-Pb dating of metamorphic and magmatic rocks.
467 Tectonics 26 TC 3014. doi:http://dx.doi.org/10.1029/2006TC002083
468 Tapponnier, P., Lacassin, R., Leloup, P.H., Schärer, U., Zhong, D., Liu, X., Ji, S., Zhang, L.,
469 Zhong, J., 1990. The Ailao Shan-Red River metamorphic belt: Tertiary left-lateral shear
470 between Indochina and South China. Nature 343, 431-437.
471 Veizer, J., 1992. Depositional and diagenetic history of limestones: stable and radiogenic
472 isotopes in: Clauer, N., Chaudhuri, S. (Eds.), Isotopic signatures and sedimentary
473 records, Springer-Verlag, Berlin, pp 13-68.
474 Yui, T.F., Khin Zaw, Wu, C.M., 2008. A preliminary stable isotope study on Mogok ruby,
475 Myanmar. Ore Geol. Rev. 34: 182-199
476 Zheng, Y.F., 1991. Calculation of oxygen isotope fractionation in metal oxides. Geochim.
477 Cosmochim. Acta 55, 2297-2307.
478 Zheng, Y.F., 1995. Oxygen isotope fractionation in magnetites: structural effect and oxygen
479 inheritance. Chem. Geol. (Isotope Geosciences Section) 121, 309-316.
480 Zheng, Y.F. 2011. On the theoretical calculations of oxygen isotope fractionation factors for
481 carbonate-water systems. Geochem. J. 45, 341-354.
482
483
484
485
486
487
488
489

490 **FIGURE CAPTIONS**

491

492 **Figure 1.** Vietnamese spinels from Luc Yen and An Phu mining districts. A- Spinel (Spl) in
493 a calcitic (Cal) marble, Cong Troi deposit. B- Spinel associated with edenite (Ed) and
494 phlogopite (Phl) in a marble from Cong Troi deposit. C- Octahedral spinel associated with
495 calcite (Cal). D- Gem crystals of pink spinel in a calcitic (Cal) marble. Photographs A-B:
496 Giuliani G ; C-D: Pardieu V.

497

498 **Figure 2.** Location of the main spinel deposits in south-east Asia (modified from Mattauer et
499 al. 1999).

500

501 **Figure 3.** Geological map showing the major tectonic domains of the Red River Shear Zone
502 in northern Vietnam with locations of the main spinel occurrences and deposits (modified
503 from Garnier 2003).

504

505 **Figure 4.** Quasi-histogram of $\delta^{18}\text{O}$ (‰ VSMOW) for 32 specimens from three deposits,
506 respectively An Phu, Cong Troi and Bai Son, in northern Vietnam with a wide range of
507 colours (see ESM Table 1 for data and details). Note the wide spread of values ($\delta^{18}\text{O} > 12\text{‰}$)
508 and the two strong and narrow modes, at $\sim 14\text{‰}$ (where are located the six spinels originating
509 from primary deposits) and $\sim 22\text{‰}$, where almost half of the data (15/32) occupy only one
510 tenth of the entire $\delta^{18}\text{O}$ range. Each symbol represents one $\delta^{18}\text{O}$ value of spinel.

511

512 **Figure 5.** Plot of spinel $\delta^{18}\text{O}_{\text{sp}}$ versus calcite $\delta^{18}\text{O}_{\text{cc}}$ for two sets (each $n=3$) of primary spinel
513 samples from An Phu and Cong Troi deposits in Vietnam, two specimens from Nepal and one
514 from Tanzania; also plotted are the two data from Myanmar of Yui et al. (2008). For the
515 Vietnamese material the best-fit line (which is that shown in the Figure) is $\delta^{18}\text{O}_{\text{cc}} = 1.01 \delta^{18}\text{O}_{\text{sp}}$
516 $+3.6$, $n = 6$, $r = 0.9925$ ($> 99.9\%$) and for the entire dataset $\delta^{18}\text{O}_{\text{cc}} = 0.96 \delta^{18}\text{O}_{\text{sp}} + 4.4$, $n=11$, r
517 $= 0.9974$ ($> 99.9\%$). The mean difference between the calcite and spinel $\delta^{18}\text{O}$ data is $\Delta^{18}\text{O}_{\text{cc-sp}}$
518 $= 3.6 \pm 0.25\text{‰}$ ($n=11$).

519

520 **Figure 6.** P-T metamorphic conditions of stability for mineral associations from ruby and/or
521 spinel-bearing marbles from the Luc Yen-An Phu area in northern Vietnam (modified from
522 Garnier et al., 2008). The domain of stability of spinel is drawn in red. It is limited by the

523 equilibrium: corundum + dolomite \leftrightarrow spinel + calcite + CO₂, the equilibrium: 2spinel +
524 6corundum + clinochlore \leftrightarrow 2sapphirine + 4H₂O, and the isochores of the fluids calculated
525 for the CO₂-bearing fluids trapped by gem ruby during the retrograde stage. Abbreviations:
526 An = anorthite; And = andalusite; Cc = calcite; Clin = clinochlore; Co = corundum ; Do =
527 dolomite; Dsp = diaspore; Ksp = K-feldspar; Ky = kyanite; Ma = margarite; Mu = muscovite;
528 Sill = sillimanite; spr7 = sapphirine; Sp = spinel; Zo = zoisite. Diagrams calculated with
529 TWEEQU (Berman, 1991).

530

531 **Figure 7.** Oxygen isotopic signatures of marbles from the Luc Yen and An Phu mining areas
532 (from Garnier, 2003; Garnier et al., 2008), and those from the calcite-spinel pairs from the An
533 Phu and Cong Troi deposits (this study).

534

535

536 **TABLE CAPTIONS**

537

538 **Table 1.** C-O-isotopic compositions of calcite and O-composition of coexisting spinel in
539 marbles from northern Vietnam, Nepal, Tanzania and Myanmar.

540

541

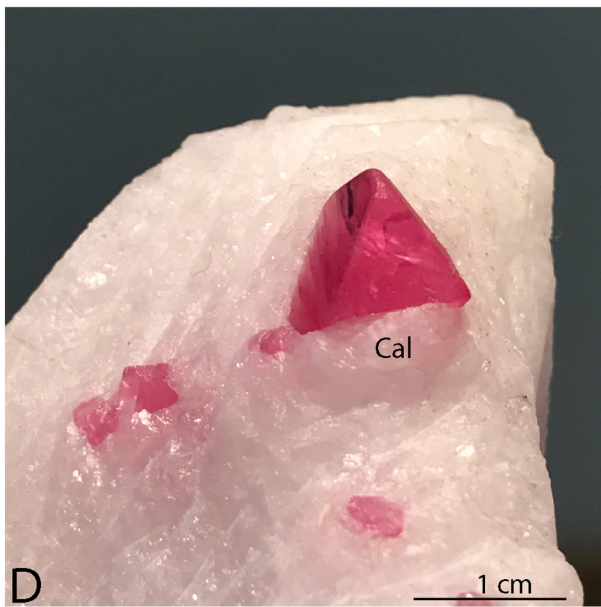
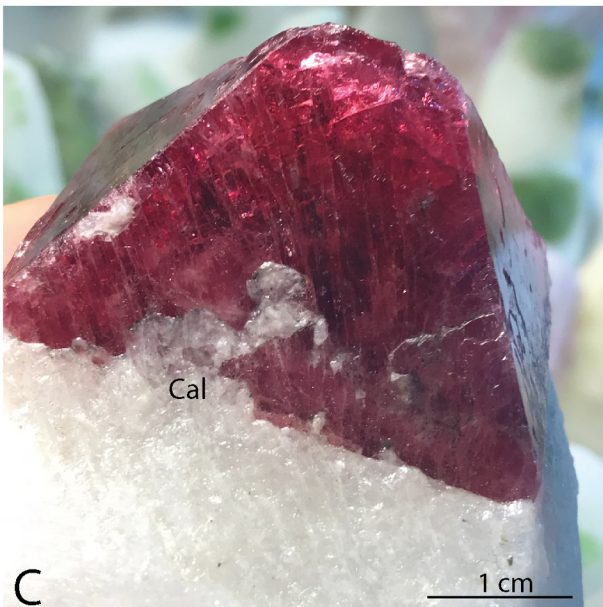
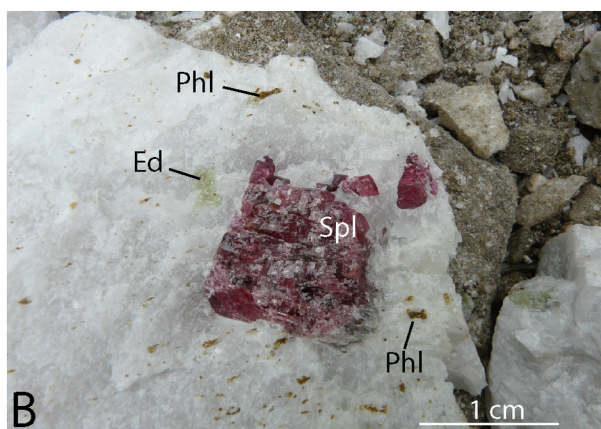
542 **SUPPLEMENTARY MATERIAL**

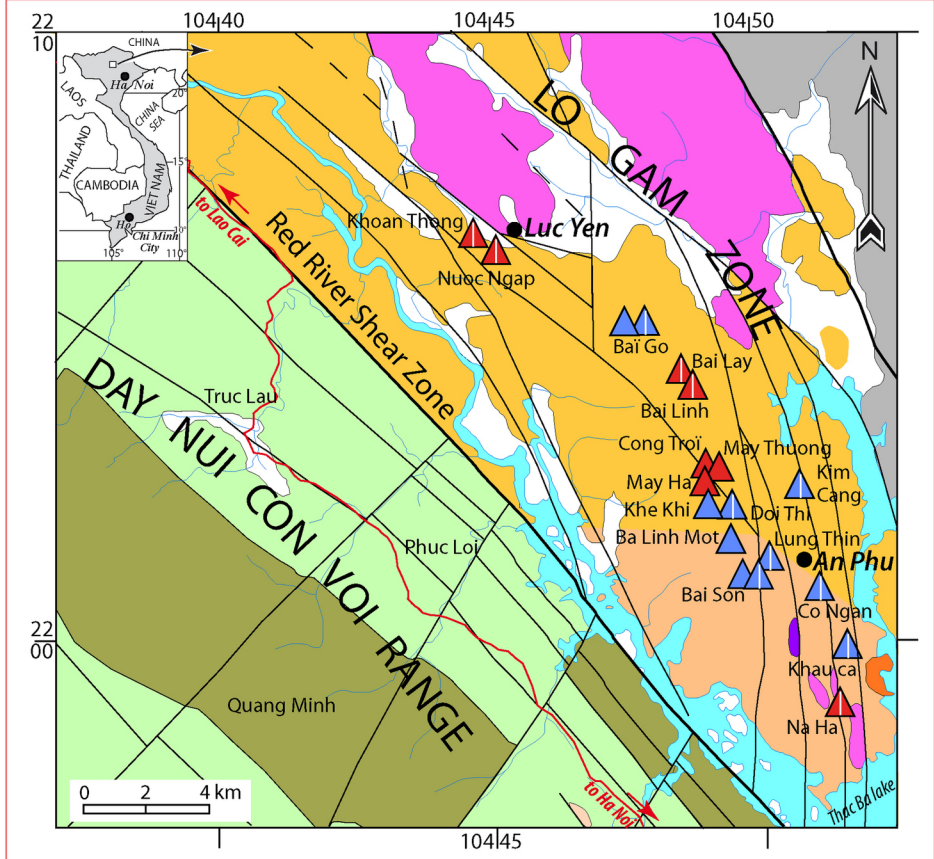
543

544 **SM Table 1.** Oxygen isotope composition (in ‰, V-SMOW) of spinels in marble deposits
545 worldwide (modified from Giuliani et al. 2017).

546

547 **SM Table 2.** (C,O) isotopic compositions of carbonates in marbles from the Luc Yen and An
548 Phu areas (Garnier 2003; Garnier et al. 2008).





Lo Gam Zone

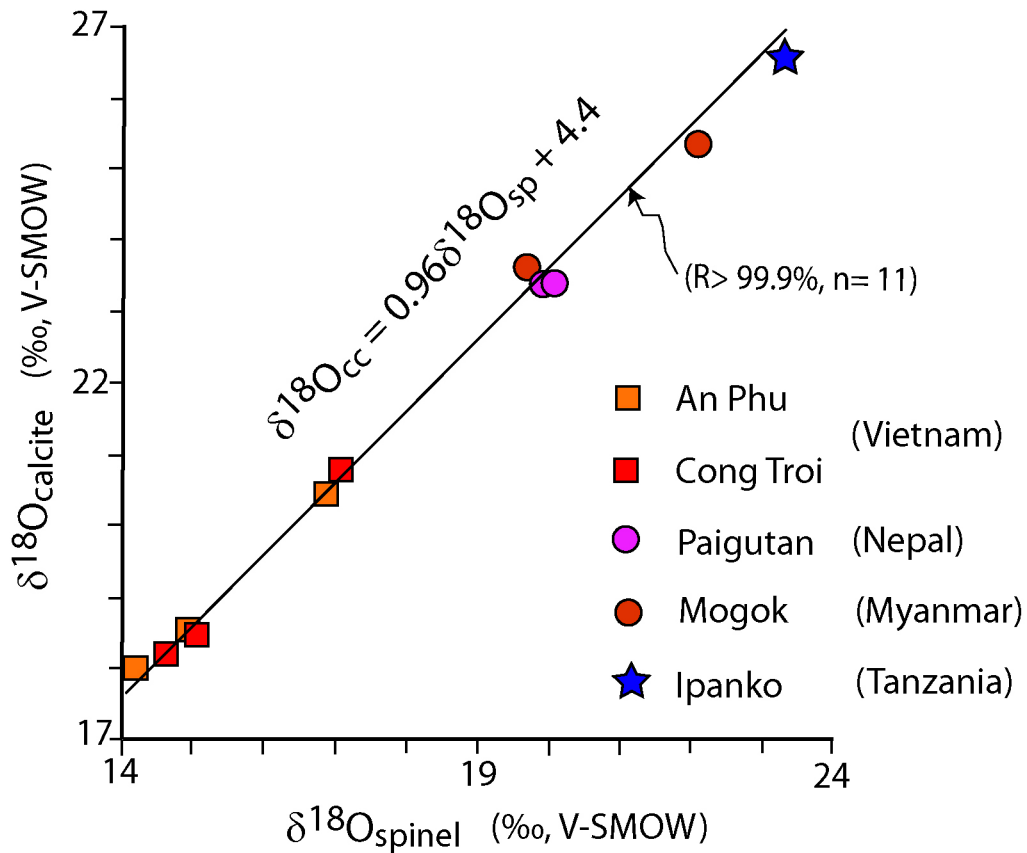
- Quaternary sediments
- Dai Thi Formation
- An Phu Formation
- Thac Ba Formation
- Nui Chua Complex
- Hia Bioc Complex
- Phia Ma Complex

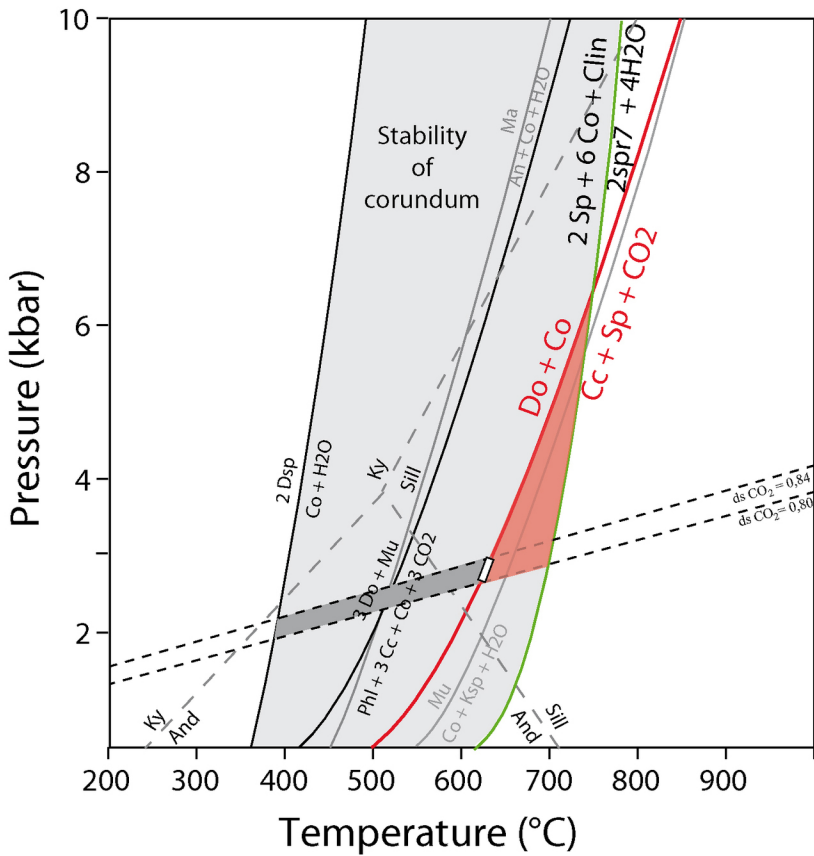
Day Nui Con Voi Range





- Quaternary sediments
- Ngoi Chi Formation
- Nui Voi Formation
- Tan Huang granite
- road
- fault
- lake and river

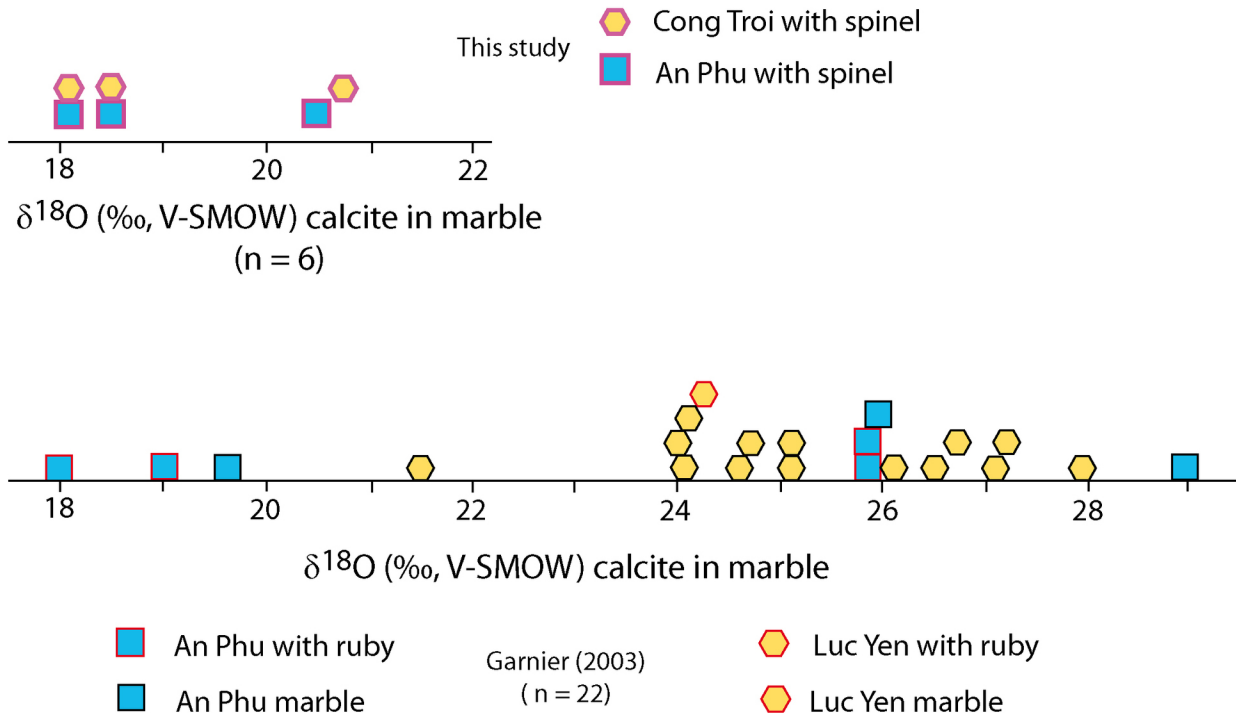
Spinel deposits

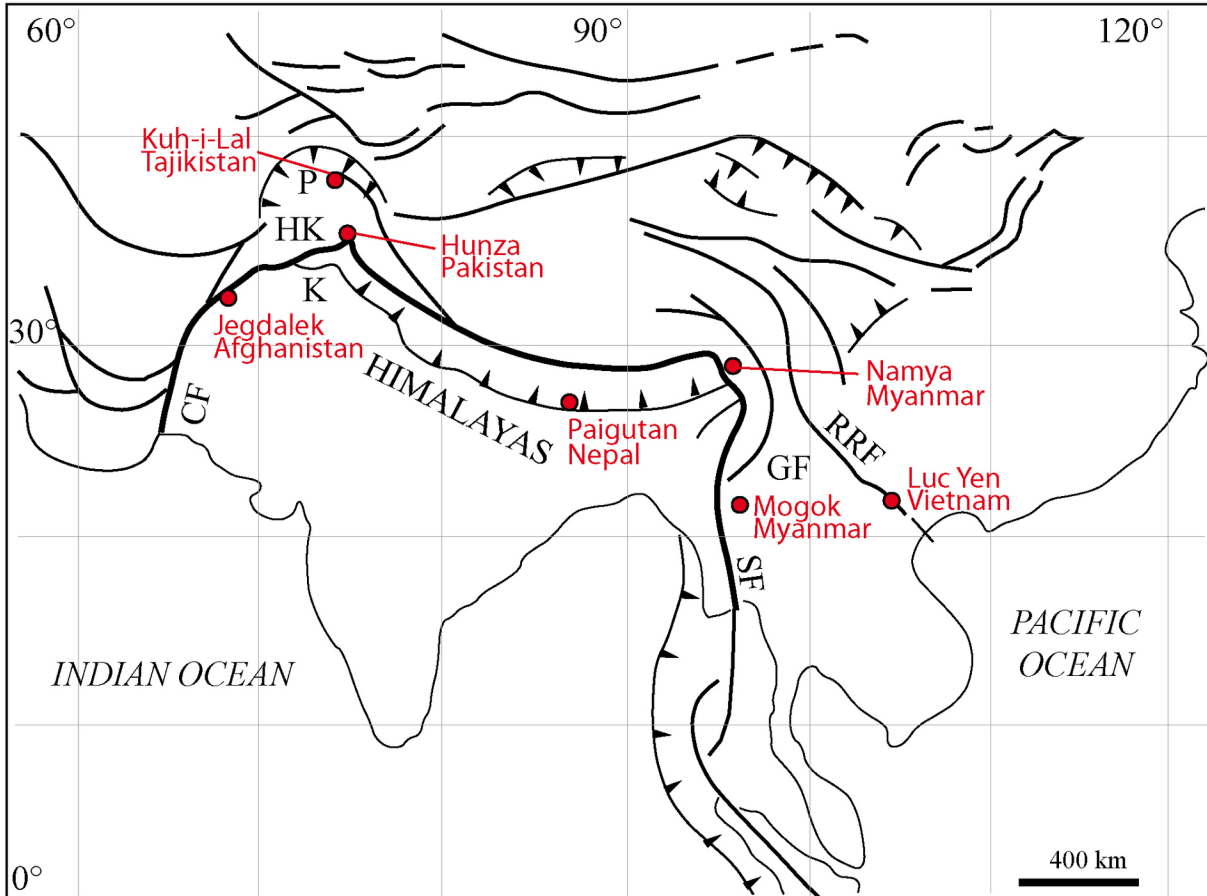
- Primary deposits
- blue
- Placers
- town, village





-  Conditions of gem ruby crystallisation in Vietnam
-  Domain of ruby stability in marbles
-  Isochores of fluid inclusions trapped in gem ruby
-  Domain of spinel stability in marble





● spinel deposit



main thrust



main fault

main faults (F) : CF= Chaman, GF= Gaoligong, SF= Sagaing, RRF= Red River

main tectonic blocks : HK= Hindu Kush, K= Kohistan, P= Pamir

Country	Deposit	Sample	colour sample	Mineral						References
				Calcite		% calcite	Spinel $\delta^{18}\text{O}$	Calcite-Spinel		
				$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{18}\text{O}$ (‰ V-SMOW)			$\Delta^{18}\text{O}_{\text{cc-sp}}$ (‰ V-SMOW)	mean $\Delta^{18}\text{O}_{\text{cc-sp}}$	
Vietnam	An Phu	AP2	pale purple	0.77	18.1	99.7	14.2	3.9	3.73 ± 0.15	this work
	"	AP4	red	2.66	20.5	99.8	16.8	3.7		"
	"	Apa	deep purple	0.41	18.5	97.7	14.9	3.6		"
	Cong Troi	VIET 31	pale pink	0.56	18.16	99.9	14.7	3.46	3.64 ± 0.16	"
	"	VIET 32	dark brown	0.87	20.75	81.7	17.0	3.75		"
	"	VIET 33	red	2.06	18.51	100	14.8	3.71		"
Nepal	Paigutan	G85-1	reddish	2.66	23.36	100	19.8	3.56	3.45 ± 0.18	"
	"	G85-2	pink	2.68	23.24	100	19.9	3.34		"
Tanzania	Ipanko	IPAN2	pink	3.88	26.69	100	23.3	3.39	3.39	"
Myanmar	Mogok	K-4	red	2.3	25.3	?	22.2	3.1	3.55 ± 0.64	Yui et al. (2008)
		K-5	red	2.1	23.7	?	19.7	4.0		"