# Journal Pre-proofs

Prograde and retrograde metasomatic reactions in mineralised magnesium-silicate skarn in the Cu-Au Ertsberg East Skarn System, Ertsberg, Papua Province, Indonesia

Melanie J. Sieber, Frank J. Brink, Clyde Leys, Penelope L. King, Richard W. Henley

Please cite this article as: M.J. Sieber, F.J. Brink, C. Leys, P.L. King, R.W. Henley, Prograde and retrograde metasomatic reactions in mineralised magnesium-silicate skarn in the Cu-Au Ertsberg East Skarn System, Ertsberg, Papua Province, Indonesia, *Ore Geology Reviews* (2020), doi: https://doi.org/10.1016/j.oregeorev.2020.103697

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
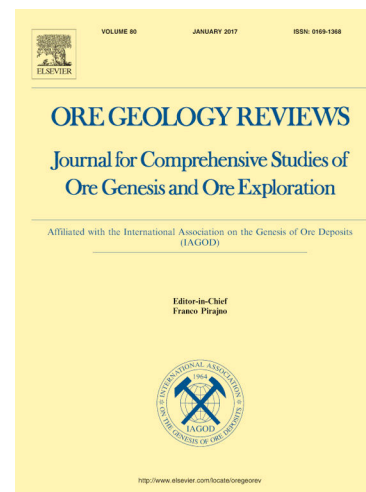
1 **Prograde and retrograde metasomatic reactions in mineralised magnesium-silicate**

2 **skarn in the Cu-Au Ertsberg East Skarn System, Ertsberg, Papua Province, Indonesia**

3 [1,2]*Sieber, Melanie J., [3]Brink, Frank J., [4]Leys, Clyde, [1]King, Penelope L. and [5]Henley, Richard

4 W.

5 1. Research School of Earth Science, The Australian National University, Canberra ACT 0200,

6 Australia

7 2. Present address: University of Potsdam, Institute for Mineralogy, Potsdam, Germany

8 3. Centre for Advanced Microscopy, The Australian National University, Canberra ACT 0200,

9 Australia

10 4. P.T. Freeport Indonesia, Tembagapura, Papua, Indonesia

11 5. Department of Applied Mathematics, Research School of Physics, The Australian National

12 University, Canberra ACT 0200, Australia

13 * Corresponding author, melanie.sieber@uni-potsdam.de, +49 331 977 5671

14

## Abstract

16 The 2.7-2.9 Ma Ertsberg East Skarn System (EESS) is a world-class Cu-Au skarn that formed within

17 and adjacent to an intrusion within a paleodepth of 0.5 km and > 2.5 km. Its economic mineralisation

18 developed by sustained reaction of magmatic fluid with contact metamorphosed siliciclastic and

19 carbonate rocks at the margin of the adjacent Ertsberg quartz monzodiorite intrusion. Based on high-

20 resolution mineral mapping, chemical analysis and thermodynamic calculations, the multistage

21 formation processes of the exoskarn components of the EESS are examined in the context of

22 changing pressure, temperature, fluid composition and fluid phase. We show that contact

23 metamorphism of dolomitic sediments occurred at $51 \pm 5$ MPa, between 700 °C and 800 °C and in the

24 presence of a $H_2O$-$CO_2$-fluid containing ~10 to ~70 mol% $CO_2$. This prograde metamorphism formed

25 a forsterite + diopside + calcite + phlogopite + spinel assemblage. Such forsterite-dominated skarns

26 account for ~55 vol.% of the EESS exoskarns. Rare pargasite (previously unrecognized in this

27 deposit) formed locally in the metamorphosed carbonate sequence where the protolith was composed

28 of supratidal evaporites with dolomitic carbonate and interlayered calc-silicate rocks. The subsequent

29 flux of a lower pressure magmatic *gas* containing $SO_{2(g)}$ caused sulphate metasomatism. This high

30 temperature gas alteration of the metamorphic assemblage also caused skarn Cu-Fe-sulphide

31 mineralisation. The influx of a $SO_2$ gas through fracture permeability occurred at a temperature

32 between ~600 and 700 °C and caused calcite to be replaced by anhydrite, with the coupled release of

33 $H_2S_{(g)}$. This *in-situ* release of $H_2S_{(g)}$ scavenged trace Cu from the gas phase to deposit Cu-Fe-

34 sulphides, which make the economic value of the distinct. We demonstrate that the formation of

35    metal sulphides within forsterite skarns of the Ertsberg East Skarn System required a minimum flux of

36    ~1,050 Mt $SO_{2(g)}$ and show that volcanic degassing may have occurred over a time span of ~3,900

37    years. As the system waned, the ambient fluid resulted in partial retrograde serpentinization of olivine

38    and diopside without carbonation, and at temperatures sufficiently high to preserve anhydrite.

39    **Keywords**

40    Porphyry Cu-Au deposit

41    Magnesium silicate skarn

42    Pargasite

43    Gas-solid reaction

44    Sulphate metasomatism

45

# 1   Introduction

47    The Ertsberg East Skarn System (EESS), a world-class exo- and endoskarn-hosted copper and gold

48    deposit is located near to the giant Grasberg porphyry Cu-Au deposit in eastern Indonesia (Fig. 1)

49    (Leys et al., 2012). Mineralisation in the EESS is superimposed on the northern margin of the

50    Ertsberg intrusion as well as on a large mass of siliciclastic and carbonate units of the Cenozoic New

51    Guinea Limestone Group that were metamorphosed to calcium-magnesium silicate skarns during

52    emplacement of that stock (Kyle et al., 2014). Such intrusion-related skarn systems have

53    complex mineral associations (Einaudi and Burt, 1982; Pirajno, 2013) due to primary

54    geochemical variations across their host stratigraphy and the extent of metasomatic alteration. Contact

55    metamorphism of the New Guinea Limestone Group produced Ca-rich garnet-diopside silicate rocks

56    and forsterite marbles through decarbonation and dehydration reactions (Turner, 1981). These

57    metamorphic assemblages have been comprehensively described by Gandler (2006) emphasizing

58    how the variability of skarn mineralogy is related to both protolith composition and temperature

59    via proximity to the intrusion contact. Subsequent magmatic fluid flux along fracture arrays

60    through the contact metamorphosed carbonate sequence led to skarn mineralisation (Gandler,

61    2006; Henley and Seward, 2018; Meinert et al., 1997). Fluid inclusion and sulphur isotope

62    data  imply that the skarn mineralisation developed at temperatures above ~600 °C (Baline, 2007;

63    Gibbins, 2006; Harrison, 1999; Mertig, 1995; Mertig et al., 1994).

64    In the EESS, Henley et al. (2017) showed that the mineralised calc-silicate mineral

65    assemblages dominated by garnet (andradite and grossular), anorthite and anhydrite formed through

66    poly-diffusive gas-solid reactions as a consequence of the flux of magmatic gas through

67    calcareous marble units. However, new data provided from extensive proprietary drilling reveal that

68    such garnet-bearing skarns comprise less than 5 % rock volume (vol.%) of the total mineralised

exoskarn skarn bodies in the EESS. Thus, an understanding of the fluid-rock metasomatic reactions at a scale of $km^3$ requires analysis of the much more abundant, mineralised anhydrite-magnetite-forsterite skarn. These Mg-rich mineralised skarns make up ~55 vol.% of the total ~0.93 $km^3$ volume of the EESS exoskarns and their petrogenesis is the focus of this study. The remaining volume (~0.36 $km^3$) of mineralised exoskarn assemblages is comprised of other co-genetic assemblages including magnetite-rich and hornfels skarns. The mass of EESS metasomatised and mineralised sedimentary rock is at least 2,600 Mt (the estimated tonnage of EESS exoskarns).

In this paper, we provide new geochemical and mineralogical data for the dominant Mg-rich silicate skarn assemblages enabling a comprehensive model to be developed for the succession of fluid-rock interaction processes that occurred from contact metamorphism, through fluid release from high-level intrusions to subsequent retrograde reactions. The samples analysed here are exoskarns meaning contact metamorphic skarns outboard of the associated igneous intrusion. However, we have otherwise not adopted any of the empirical classification schemes that are used in lithological mapping to distinguish mineralisation types through individual deposits (Meinert et al., 2005). Rather we have focussed on distinguishing first-order variations in overall chemistry (Ca-rich vs. Mg-rich), that are related to protolith composition, and consequent, second order variations in mineralogy (Ca-silicate skarns vs. Mg-silicate skarns). We have developed a new bulk geochemical model for the large-scale metasomatic processes that converted contact metamorphic skarn assemblages to oxidised sulfate-rich mineralised rock with CuFe-sulphides as a by-product. Understanding of skarn formation and mineralisation extends beyond the economically significant skarns at Ertsberg and elsewhere because the high temperature fluid-rock reaction processes discussed here are also applicable to the interpretation of processes beneath modern active volcanoes, such as Vesuvius (Italy) and Lascar (Chile), where mineralised skarn ejecta are found (Fulignati et al., 2001; Matthews et al., 1996).

## 2 Geological setting

The formation of the Ertsberg East Skarn System (EESS) is a consequence of emplacement of the 2.9 to 2.7 Ma Ertsberg intrusion into regionally extensive Cenozoic New Guinea Limestone Group sediments (Fig. 1) (Kyle et al., 2014). The Erstberg intrusion comprises a quartz monzonite to quartz monzodiorite stock that was emplaced at ≤2 km depth into the Cenozoic and older sedimentary formations (McMahon, 1994). The New Guinea Limestone Group is comprised of mixed siliciclastic and carbonate units, interpreted to have been deposited on a shallow marine shelf. One of the principal stratigraphic units that developed into mineralised skarns within the New Guinea Limestone Group is the folded, ~0.3 km thick Paleocene Waripi Formation comprised of dolostone, siltstone, dolomitic to sandy limestone, calcareous sandstone, calcareous mudstone, sandy dolomite and sandstone (Gandler, 2006; Meinert et al., 1997). Towards the top of the Waripi Formation the abundance and thickness of sandstone increases and anhydrite nodules are present as

105 a minor component (Gandler, 2006). The Waripi Formation is overlain by Eocene Faumai
106 Formation massive limestones and sandstones (Gandler, 2006; Meinert et al., 1997).

107 For this study, a suite of skarn samples was provided by PT Freeport Indonesia from a single
108 underground drill hole (TE06-24) through the Deep Mill Level Zone of the EESS. Based on
109 reconnaissance analyses, two samples (CS1 and FM1) were selected that best exhibited distinct
110 compositional variations related to the sedimentary precursor, sulphide-sulfate mineralisation and
111 retrograde alteration. CS1 and FM1 present samples of altered Waripi Formation at a depth of
112 ~1,600 m below the present surface, and located 9.5 m (CS1) and 98.7 m (FM1) from the
113 Ertsberg intrusion contact (Fig. 1b and c). Part of sample CS1 (TE06-24: 270.6 m) was described as
114 an altered and mineralised calc-silicate skarn (Henley et al., 2017). In this study, we
115 investigated the contiguous lower part of that sample that has a contrasting Mg-silicate
116 assemblage and the contact zone between the calc-silicate and the Mg-silicate assemblages. New
117 data for phase relations in this distinct assemblage is provided as a basis for further refining
118 the understanding of metasomatic processes during subsequent mineralisation. Based on a second
119 sample (FM1), new analytical data is also provided for mineral assemblages in the forsterite marble
120 sequence that makes up ~55 vol.% of the exoskarn component of the EESS deposit and which was
121 subsequently altered to a Mg-silicate + anhydrite assemblage with Cu-Fe-sulphides (sample FM1;
122 TE06-24: 359.9 m).

## 3    Analytical methods and thermodynamic calculation

### 3.1    Analytical methods

125 Polished thick sections of CS1 and FM1 were prepared using dry cutting and water-free polishing
126 paste. Mineral phases were identified using a JEOL 6610A scanning electron microscope (SEM)
127 equipped with an Energy Dispersive spectroscopy (EDS) system at the Research School of Earth
128 Sciences, Australian National University (ANU). Selected mineral phases were quantitatively
129 analysed using a JEOL JXA-8530F Plus Microprobe equipped with 5 wavelength dispersive
130 spectrometers (WDS) at the Centre for Advance Microscopy (CAM), ANU. We used a 50 nA probe
131 current and an accelerating voltage of 8 kV to improve spatial resolution. The system was calibrated
132 against well-characterised standards including periclase (Mg), diopside (Ca), sanidine (Si, K),
133 hematite (Fe), albite (Al), $CaF_2$ (F), albite (Na), rutile (Ti) and chromite (Cr). Almandine, pyrope and
134 chlorite were used as secondary standards to monitor measurement performance. The FEI Quanta
135 650F "™QEMSCAN" (Quantitative Evaluation of Minerals) at CAM was used to collect EDS-Field
136 Emission (FE)-SEM maps for visualising the mineral distribution. Mapping was performed using
137 10 nA probe current, 15 kV accelerating voltage, a count rate of approximately 420,000 counts per
138 second, 3,000 counts/pixel and a step size of 9.9 μm. ™QEMSCAN uses a EDS library to
139 automatically recognise mineral phases. In addition, ™QEMSCAN mineral mapping was calibrated

4

140  by independent SEM spot analyses allowing measured mineral compositions to be correlated  with

141  mineral phases. Mineral proportions within a given field of interest were computed with  the

142  ™QEMSCAN software.

143  3.2 Thermodynamic modelling

144  For the purposes of thermodynamic modelling and determination of the temperature condition and the

145  $CO_2$-$H_2O$ fluid composition during contact metamorphism, the bulk rock compositions were

146  constrained from the phase abundances established in the ™QEMSCAN maps and the composition of

147  mineral components (Table 1). The bulk rock compositions were calculated considering the

148  proportion and composition of mineral phases with abundances >1 area% in the ™QEMSCAN map.

149  Using the bulk compositions (listed in Table 1) to reconstruct the composition of the sedimentary

150  precursor assumes negligible chemical gains or losses, except for variations of the volatile

151  components, during prograde and retrograde reactions (Stage 1, 2 and 3). This assumption is

152  reasonably well sustained for sample FM1, because the reconstructed bulk composition of FM1 is in

153  accordance with unmetamorphosed and unaltered dolomitic sandstone and limestone of the Waripi

154  Formation (Gandler, 2006) (Fig. 2). Accordingly, the bulk composition of FM1 implies a sandy

155  dolostone as sedimentary precursor. However, the Mg-rich-silicate and the contact-zones of sample

156  CS1 (hereafter referred to as CS1-Mg-rich-silicate and CS1-contact-zone respectively) are enriched

157  in e.g. Na, K, Al and Mg+Fe compared to unmetamophosed rocks of the Waripi Formation reported

158  by Gandler (2006) (Fig. 2 and Table 1 in the supplementary information).

159  Isobaric temperature-$X_{CO_2}^{fluid}$ pseudosections were computed with the Perple_X thermodynamic

160  software package (version 6.8.4; Connolly (2009)) using the CORK equation of state for the fluid and

161  thermodynamic data from Holland and Powell (1991); Holland and Powell (1998, 2011). $X_{CO_2}^{fluid}$ is

162  defined as the mole fraction of $CO_2$ in a $CO_2$-$H_2O$-bearing fluid. Solid solution models employed in

163  the calculations include: biotite, chlorite, chloritoid, cordierite, garnet, melt, mica, orthopyroxene,

164  staurolite after White et al. (2014); sapphire after Wheller and Powell (2014); feldspar after Fuhrman

165  and Lindsley (1988); carbonate after Holland and Powell (2003); clinopyroxene and olivine after

166  Holland and Powell (1998); spinel after White et al. (2002) and clino- and orthoamphibole after

167  Diener and Powell (2012). The volatile-free, bulk compositions of the Mg-silicate skarns were

168  modelled in the $SiO_2$-$Al_2O_3$-FeO-MgO-CaO-$Na_2O$-$K_2O$-system and assume connected porosity with a

169  single-phase $CO_2$-$H_2O$ fluid at 51 MPa. Note, that minor amounts of $Na_2O$ (~4 ppm) in the bulk

170  composition of FM1 were omitted in the thermodynamic modelling. For assumptions and reasoning

171  of this pressure (51 MPa) the reader is referred to section 5.1.1.

172  # 4    Mineral chemistry

173  Below, we provide a petrographic description of two Mg-silicate skarn samples (CS1 and FM1) from

174  the East Ertsberg Skarn System based on high resolution ™QEMSCAN maps and EPMA mineral

175    analysis (Table 1).

## 4.1    Sample FM1

177    The section of sample FM1 consists of mostly anhydrite (76 area%), significant serpentine (15
178    area%), some magnetite and forsterite and traces of phlogopite and sulphides (Fig. 3; Table 1).
179    This assemblage has neither diopside nor brucite although both phases occur in adjacent parts of the
180    rock sequence indicating a primary variability of Ca/Mg ratio in the sediment or variations in the fluid
181    composition. The ™QEMSCAN maps of FM1 show an equigranular texture of anhydrite and
182    partially serpentinized forsterite (Mg#~95.5) with interstitial and idioblastic grains of phlogopite (Fig.
183    3a-b). Phlogopite crystals are up to ~1 mm long, homogeneous with Mg#~92.3 and rarely occur as
184    inclusions in olivine (Fig. 3c).

## 4.2    Sample CS1

186    Sample CS1 shows a contact between an upper calc-silicate unit and a lower, Mg-rich unit marking
187    compositional variations in the sedimentary precursor and subsequent alteration reactions (Fig. 4a).
188    The contact zone between the upper *CS1-calc-silicate* (orange-brown) and lower *CS1-Mg-rich-
189    silicate* (green) is well-defined in the hand specimen by a change in colour (Fig. 4a). The *CS1-
190    calc-silicate* is the subject of a previous study and it contains garnet (andradite and grossular),
191    anorthite, anhydrite, clinopyroxene, epidote, chalcopyrite, orthoclase, calcite, apatite and minor
192    quartz (Henley et al., 2017).

### *4.2.1    CS1-contact-zone*

194    The contact-zone between the *CS1-calc-silicate* and *CS1-Mg-rich-silicate* is ~1 cm wide and light
195    green. The upper part of the contact zone, *CS1-upper-contact*, is dominated by diopside (80 area%),
196    with much less phlogopite (12 area%) and pargasite, minor anhydrite, and trace spinel, garnet and
197    bornite (each ≤0.1 area%; Table 1). The lower part of the contact zone, *CS1-lower-contact*, is
198    dominated by phlogopite (54 area%) and contains lesser pargasite (22 area%) and diopside (16
199    area%), with minor Al-spinel and anhydrite and trace bornite, Cr-spinel, hematite, magnetite,
200    olivine, serpentine and garnet (each ≤0.6 area%; Table 1). The distinct change in mineral assemblage
201    and mode within the contact zone is interpreted to reflect compositional variation in the sedimentary
202    precursor together with different degrees of metasomatic overprint (see *5. Discussion*).

203    The upper contact zone contains tabular phlogopite enclosed by irregularly-shaped diopside. The
204    grain size and abundance of phlogopite increases towards the Mg-rich silicate part of sample CS1
205    (Fig. 4b and 5a) and phlogopite crystals show an irregular habit in the lower contact zone (Fig. 5a-b).
206    Throughout the entire contact zone, spinel has irregular grain boundaries and is enclosed in phlogopite
207    implying partial replacement of spinel by phlogopite. Poikiloblasts of medium-grained Na-amphibole
208    (pargasite) occur predominantly in axial plane cleavage (subparallel to the stratigraphic contact

between the calc-silicate and the Mg-rich silicate rocks) that cuts across an anhydritic lamina within the contact zone (Fig. 4b). This lamina may be a primary feature of the evapouritic protolith. Pargasite also occurs within the *CS1-Mg-rich-silicate* (Fig. 5c). Pargasite grains contain inclusions of phlogopite and diopside (Fig. 5b-c). Furthermore, pargasite grains are homogeneous and have, in contrast to phlogopite crystals, a more consistent composition across the contact zone (Mg#=82.5-83.5). The abundance of diopside crystals decreases across the contact zone from the *CS1-calc-silicate* to the *CS1-Mg-rich-silicate*. Diopside grains in the contact zone are inhomogeneous and contain at least three distinct zones identified by their different contrast intensities in BSE-images (Fig. 6). Within a single diopside grain, the composition varies from Fe- and Al-rich with $100 *$ molar Mg/(Mg+Fe)=Mg# of 80.8±1.6 (2$\sigma$) and 0.22±0.01 apfu Al (apfu = atoms per formula unit; here for 6 oxygens), to an intermediate composition with Mg# of 93.2±2.2 and Al=0.08 apfu to a Fe- and Al-poor composition showing Mg# of 98.8±1.4 and Al of ≲0.1±0.1 apfu (Fig. 6). Fe and Al-rich diopside grains are low in silica (Si=1.8±0.01 apfu) and may contain some water (~0.7 wt.%) as implied by systematically low analytical totals from electron microprobe analyses.

Individual phlogopite grains are homogeneous in the contact zone, but the Mg# of phlogopite crystals changes gradually across the contact. In *CS1-lower-contact*, phlogopite crystals are richer in Mg (Mg#~92) relative to phlogopite grains close to *CS1-calc-silicate* (Mg#~90). Grains of phlogopite commonly surround Al-spinel crystals ($Mg_{0.76}Fe^{2+}_{0.26}Fe^{3+}_{0.06}Al_{1.94}O_4$; Mg#=74.5) and contain small amounts of Na (~0.03 apfu; for 11 oxygens).

### 4.2.2   *CS1-Mg-rich-silicate*

The *CS1-Mg-rich-silicate* (below the contact) is dominated by pargasite (42 area%), with significant forsterite (25 area%), some diopside, serpentine and phlogopite, minor anhydrite and trace (≤0.3 wt.%) bornite, hematite, Al-spinel, magnetite, chlorite and spadaite ($MgSiO_2(OH)_2 *$ x $H_2O$) (Fig. 5, Table 1). Forsterite, diopside and phlogopite are xenomorphic (Fig. 5b-c). Serpentine and magnetite replace forsterite (and diopside) along veinlets that are texturally unrelated to pargasite (at the bottom of Fig. 5a). Phlogopite crystals in the *CS1-Mg-rich-silicate* have high Mg# of 92 to 93 and contain some Ti ($TiO_2$=0.2 wt.%); they are homogeneous and may surround Al-spinel in places. Pargasite grains are homogeneous and have Mg# of ~83 (ranging from 82.5 to 84.2). Diopside crystals show the patchy, irregular composition seen in diopside crystals within the contact zone. Forsterite crystals display Mg zoning with highest Mg# of 96.9 in the cores (ranging from 93.4 to 98.3) and Fe-richer rims (Mg# median is 91.8; Mg# ranges from 90.9 to 95.4). Serpentine has a median Mg# of 96.7 (ranging from 95.9 to 97.8) and contain some Al when replacing diopside (Al<<0.1 apfu for 7 oxygens). Clinochlore is fibrous, fine-grained, Cr-free and has Mg# of ~95.6 and spadaite has Mg#~90.4. Fine-grained and euhedral magnetite grains within veinlets are likely formed as a result of forsterite hydration.

244     4.3     Sulphide minerals in CS1 and FM1

245   Although Cu-Fe-sulphide grains constitute <1 area% of the mineral maps (Fig. 3, 4 and 5) for the

246   studied samples (CS1 and FM1), the copper content that they contribute to the rock is responsible for

247   the economic value of the EESS. Since the unmetamorphosed protolith (sandy dolostone - limestone)

248   does not contain any copper, the presence of Cu-Fe-sulphides is testimony to the pervasive, post-

249   contact metamorphism flux of a fluid phase containing sulphur plus these metals. Cu-Fe-sulphide

250   grains are texturally associated with anhydrite (Fig. 4c). Individual Cu-Fe-sulphide grains are either

251   bornite-chalcocite solid solutions or Zn-bearing covellite (Fig. 7). Within a single sulphide grain, the

252   composition ranges between bornite and chalcocite. The compositional variability within individual

253   sulphide grains is evident in BSE-images (Fig. 7c, d) and likely reflect exsolution from Independent

254   Solid Solution (ISS) on lowering temperature below about 700 °C (Fig. 7e) (Kullerud et al.,

255   1969; Yund and Kullerud, 1966).

# 5     Discussion

257   Here we describe the evolution of the Mg-silicate skarns (CS1 and FM1) from contact metamorphism

258   of carbonate-rich sediments (Stage 1), subsequent skarn mineralisation by their reaction with a flux of

259   magmatic gas (Stage 2) and finally retrograde, hydrothermal alteration (Stage 3). The mineral

260   chemistry data for the Mg-rich silicate skarns provide the basis for determining the pressure and

261   temperature conditions (contact metamorphism – Stage 1) under which the Mg-silicates formed in the

262   Ertsberg hydrothermal system. These conditions may then be related to pressure and temperature

263   conditions during fluid flow in the subsequent stages (Stage 2 and 3) as is discussed below.

264     5.1 Stage 1: Contact metamorphism

265   In the following we argue that contact metamorphism occurred at a pressure of $51 \pm 5$ MPa and peak

266   metamorphic temperature of $750 \pm 50$ °C in the presence of a $CO_2$-$H_2O$-fluid containing between ~10

267   to ~70 mol% $CO_2$. First, constraints on the pressure during contact metamorphism will be provided.

268   Then, the mineral assemblages formed during contact metamorphism, the metamorphic temperature

269   and fluid composition are considered based on thermodynamic modelling.

270     *5.1.1   Constraints of the pressure during contact metamorphism*

271   There are two methods to constrain the confining pressure at the paleodepth of each sample. First,

272   data from Wafforn et al. (2018) and Wafforn (2017) using U-Pb zircon and garnet and U-Th/He

273   apatite ages from vertical profiling in the Grasberg deposit indicates the maximum difference in

274   elevation between the present-day surface and paleo-surface of ~1 km. Second, lake sediments that

275   are preserved immediately above the older Grasberg porphyry copper deposit (only 3 km away)

276   indicate the elevation of the paleo-surface 300,000 years before the Ertsberg deposits formed. These

277   lake sediments outcrop at 4.2 km a.s.l. (above sea level) so that we may conservatively estimate that

278    the paleo-surface was at about 4.5 km a.s.l. (Fig. 1d). Considering subsidence and compaction of the

279    lake beds at Grasberg, volcanic topography, and the low amplitude of subsequent folding and faulting

280    during uplift of the region provides an estimated uncertainty of ~0.2 km. This suggests that the

281    maximum difference between the present-day surface and paleo-surface is ~0.5 km (Fig. 1d). Since

282    the investigated drillhole samples were obtained from a depth of ~1.6 km, the paleodepth of the

283    sample is about 2.1 km below surface (Fig. 1d), equal to a lithostatic pressure of $51 \pm 5$ MPa. This

284    pressure estimate assumes densities for quartz- and carbonate-rich sediments of 2,648 kgm$^{-3}$ and 2,710

285    kgm$^{-3}$, respectively, and average porosities for sandstones of 12 vol.% and for limestones of 4.3

286    vol.% after Barrell (1914). Within uncertainty, this pressure ($51 \pm 5$ MPa) correlates well with the

287    pressure of $49 \pm 10$ MPa estimated by Henley et al. (2017) from the *CS1-calc-silicate* and

288    thermodynamic modelling.

### 5.1.2  *Contact metamorphism*

290    The thermal decomposition of sedimentary carbonate rocks releases significant amounts of $CO_2$ and

291    $H_2O$. In order to model the mineral variability caused by different fluid compositions over a range of

292    temperature, isobaric T-$X_{CO_2}^{fluid}$ pseudosections were calculated, assuming that the system was

293    saturated by an interconnected $CO_2$-$H_2O$ fluid. $CO_2$ and $H_2O$ were considered in the modelling,

294    because these are the dominant fluids released during devolatilization of carbonaceous sediments

295    such that other volatile species can be neglected in the contact metamorphic stage. Pseudosection

296    main stability fields are shown in Figure 8 and they were modelled at 51 MPa using the

297    reconstructed, volatile-free, bulk composition in respect to $SiO_2$, $Al_2O_3$, $MgO$, $FeO$, $CaO$, $Na_2O$ and

298    $K_2O$ (Table 1). The modelled, isobaric P-$X_{CO_2}^{fluid}$ pseudosection for sample FM1 shows that an

299    assemblage of calcite + forsterite + diopside + phlogopite + spinel is stable over a wide range of

300    $CO_2$-$H_2O$ fluid composition and a temperature between ~550 and ~760 °C (Fig. 8b). Within this

301    stability field, the abundance and composition of mineral phases (Table 2) are marginally sensitive to

302    changes in temperature and fluid composition. The assemblage of calcite + forsterite + diopside +

303    phlogopite + spinel is restricted by the absence of phlogopite for temperatures above ~800 °C. At T

304    $\lesssim$ 550 °C, spinel is absent and chlorite is stable (Fig. 8). We interpret this assemblage of calcite +

305    forsterite + diopside + phlogopite + spinel as the contact metamorphic paragenesis. Forsterite +

306    diopside + carbonate (calcite + dolomite) record decarbonation reactions in siliceous, dolomitic

307    marbles (e.g. Bucher-Nurminen (1982); Bucher and Grapes (2011); Skippen (1974)).

308    Calcite was efficiently replaced by anhydrite in the reaction of a high temperature fluid with the

309    contact metamorphic assemblages (see section *5.2 Stage 2: Mineralisation and alteration*). The

310    granular texture of FM1, and the idiomorphic shape of phlogopite crystals and occurrence as

311    inclusions in forsterite grains of sample FM1 (Fig. 3c), imply that phlogopite and forsterite

312    grains formed together or phlogopite formed slightly earlier. Interpretation of the modelled, high

pressure and temperature phase relations is limited to two assumptions. Firstly, local mineral-fluid equilibrium along the flow path of the fluid is assumed. Secondly, the modeling considers a closed system. The latter assumption may not be fully achieved, since Stage 2 fluid flux partially modified the bulk chemistry particularly in respect of fluid mobile elements such as S, Fe, Na and K and metals such as Cu. However, the reconstructed bulk rock composition of sample FM1 correlates reasonably to unmetamorphed parts of the Waripi Formation after Gandler (2006) for major elements such as Si, Mg+Fe and Ca (Fig. 2 and Table 1 in the supplementary information). The contact metamorphic assemblage described here is stable over a wider range of $CO_2$-$H_2O$-fluid composition up to a maximum temperature of 750 ± 50 °C (Fig. 8). Thus, we consider this temperature as the peak metamorphic temperature at a pressure of 51 ± 5 MPa. The obtained peak-metamorphic temperature is equal to the temperature during contact metamorphism reported by Henley et al. (2017) for the *CS1-calc-silicate* from the same drill core.

At 750 ± 50 °C and 51 ± 5 MPa, an equilibrium mineralogy of forsterite, pargasite, diopside, phlogopite and some calcite and spinel could be modelled for the reconstructed bulk composition of the *CS1-Mg-rich-silicate* (Fig. 8a). The reconstructed bulk composition of the *CS1-Mg-rich-silicate* and the *CS1-contact-zone* show higher Na, K, Al and Mg+Fe compared to the overall composition of the sedimentary units of the Waripi Formation (Fig. 2 and Table 1 in the supplementary information). The chemical variation is interpreted to reflect small-scale mineralogical variations in the sedimentary precursor in combination with element transport during rock-fluid interaction. The correlation between the modelled peak metamorphic assemblage of forsterite, pargasite, diopside, phlogopite and some calcite (fully replaced by anhydrite during Stage 2) and spinel to the present assemblage indicate minor gains or losses of elements. However phlogopite crystals in the *CS1-contact-zone* are irregular shaped and corroded, and the Mg# of phlogopites gradually increases from the calc-silicate towards the Mg-silicate zone of CS1. This suggests that an alternative interpretation for these systematic changes may be compositional variations within the sediment or related to element transport across the contact zone. Also, in the *CS1-contact-zone* anhydrite (as a replacement of calcite) and associated Cu-Fe-sulphides occur together with minor pargasite (Fig. 4c and 5c). These distinctive Na-rich areas in the *CS1-contact-zone* raise questions about the source of the sodium required for pargasite formation. Pargasite is most likely a prograde metamorphic phase (Stage 1) because it is commonly found in K-Mg-rich laminae indicative of evapourite-rich layers in the metasediments. We rule out pargasite formation during Stage 2 because Na and K concentrations are too low in magmatic fluids ($10^{-3}$ to $10^{-5}$ mol/kg; Henley and Seward (2018)). Around 2.5 wt% halite (NaCl) and 2 wt% sylvite (KCl) in the sedimentary precursor are sufficient to contribute the amount of Na and K needed to form the observed amount of pargasite and phlogopite in the Mg-silicate CS1. This mass-balance calculation assumes negligible modification of the bulk rock composition and suggests that the carbonate-quartz-kaolinite-halite-sylvite sediment was a minor part of a lagoonal sedimentary

349    sequence. Figure 4c and 4b shows that anhydrite and Cu-Fe-sulphide grains, with some void space,
350    infill a weak axial planar cleavage in the folded pargasite-rich lamellae through the contact zone. This
351    textural relationship further supports the interpretation of pargasite as a Stage 1 contact metamorphic
352    mineral formed in a Na-bearing protolith. The stability of pargasite in the modelled phase diagram
353    (Fig. 8a) demonstrates that pargasite is stable up to peak metamorphic PT-conditions. Pargasite has
354    not been previously reported at Ertsberg, but it has been reported as a prograde phase in
355    metacarbonates (e.g. Proyer et al. (2008); Satish-Kumar et al. (2001); Thu and Enami (2018)) and it
356    may form during metamorphism of sodic evaporite-bearing sequences (Pirajno, 2018; Warren,
357    2016; Zhu et al., 2015). All these observations point towards the formation of pargasite during
358    prograde metamorphism (Stage 1).

## 5.2 Stage 2: Mineralisation and alteration

360    Economic mineralisation within the EESS contact metamorphic skarns is caused by reaction of a high
361    temperature fluid during Stage 2 with the mineral assemblages that developed during Stage 1. First,
362    we provide geologic and geochemical evidence to demonstrate that the fluid in Stage 2 was derived
363    primarily from a magmatic source. Second, we establish the pressure and temperature range during
364    Stage 2 alteration and mineralisation of the contact metamorphosed carbonate sequence and show that
365    the fluid must have behaved as a low-density fluid (gas) in fracture arrays to produce the Cu-rich
366    skarn resources. Third, we discuss the reactions that replaced calcite with anhydrite and deposited
367    Cu-Fe-sulphides through reaction of the contact metamorphic assemblage with a flux of a magmatic
368    gas.

### 5.2.1 Role for magmatic fluids

370    Carbonate grains are (partially to completely) replaced by anhydrite in Stage 2. Some relicts of calcite
371    have been observed in the calc-silicate part of sample CS1 (Henley et al., 2017). Furthermore, powder
372    X-ray diffraction data of altered Waripi Formation drill-core samples located less than ~90 m
373    from sample FM1 indicate the presence of Mg-Fe-Ca-carbonates such as calcite, dolomite, magnesite
374    and siderite. While the Waripi Formation contains some sedimentary anhydrite nodules
375    (Gandler, 2006; Kyle et al., 2014), most anhydrite formed during replacement of
376    contact metamorphosed carbonates in Stage 2. This is indicated by the high abundance of anhydrite
377    in sample FM1 and the textural association of anhydrites and sulphides. Furthermore, sulphur
378    isotopic data for sulphide and anhydrite grains within veins from the Grasberg Intrusive Complex
379    and the EESS reveal component contributions from sulphur-bearing country rocks (e.g. the anhydrite
380    nodules in the New Guinea Limestone Group) and from a deep magma source, whereby the latter
381    becomes more significant over time (Gibbins, 2006). For these reasons, it is necessary to access a
382    larger reservoir of sulphur to form the abundant Stage 2 anhydrite and sulphides found throughout
383    the EESS. This is resolved through oxygen isotope data by recognizing that the $H_2O$ in the Stage

384 2 mineralising fluid was primarily derived from an underlying magmatic complex (Gibbins, 2006)

385 as might be anticipated because of its porphyry copper system origin (Henley and Seward, 2018).

386 The Ertsberg East Skarn System (EESS) lies adjacent to the large, monzodioritic Ertsberg Intrusion

387 that was emplaced over a period of up to 300,000 years (Cloos and Sapiie, 2013; Leys et al.,

388 2012; Macdonald and Arnold, 1994; Meinert et al., 1997; Mertig et al., 1994;

389 Paterson and Cloos, 2005; Pollard and Taylor, 2002). No specific evidence is preserved of

390 any eruptive activity relating to its near-surface (<0.5 km) emplacement. Nevertheless, the extensive

391 EESS alteration and mineralisation that extends to the present surface implies that the mineralised

392 skarn system underlay a large area of solfataric alteration at the paleo-surface, as is commonly

393 observed in quiescently degassing magmatic systems today. Such massive fluid flow requires the

394 maintenance of a permeable array of faults and fractures such as observed throughout the EESS

395 (Leys et al., 2012).

396 ### 5.2.2 Pressure-temperature and phase relations of the fluid

397 The fluid of Stage 2 had a temperature of $\gtrsim$ 600 °C based on fluid inclusion homogenisation

398 temperatures (Baline, 2007) which is consistent with the upper temperature limit of 750 ± 50 °C for

399 contact metamorphism assumed in this paper. At the samples' estimated paleo-depths (2.1 ± 0.2 km),

400 an assumption of a mean density of the overlying sediments provides an upper limit on lithostatic

401 pressure of 51 ± 5 MPa (see section *5.1.1 Constraints on the pressure during contact*

402 *metamorphism*). The highest fluid pressure possible is constrained by the sum of lithostatic

403 pressure and the tensile strength of the rock (Cox, 2010). The tensile strength of rock ranges

404 from 0.5-5 MPa so that the highest fluid pressure at the sample depth was therefore a maximum of

405 56 ± 5 MPa. However, a much lower fluid pressure necessarily occurred in the magmatic fluid phase

406 as it expanded from its source to the surface (~0.1 MPa) through a fault and fracture array, since

407 $(\rho_{fluid} * g * h) < (\rho_{rock} * g * h)$ (1)

408 where $\rho$ is the density, $g$ is acceleration due to gravity and $h$ is the depth. Magmatic fluid expansion in

409 porphyry copper systems was defined by Weis (2015) and Henley and McNabb (1978) showing the

410 formation of a low density magmatic vapour plume displacing groundwater. In order to prevent

411 groundwater swamping the system, the pressure of the magmatic fluid must be above the cold water

412 hydrostatic pressure at the sample depth. This defines a minimum pressure estimate of 21.5 ± 2 MPa

413 based on the density of groundwater. Thus, the pressure of the magmatic fluid during alteration and

414 mineralisation (Stage 2) was therefore between 21.5 ± 2 MPa and 56 ± 5 MPa.

415 It has long been established that the continuum fluid in the formation of porphyry copper and related

416 deposits is a low salinity gas phase (Henley and McNabb, 1978; Weis et al., 2012); note that the

417 term 'vapour' applies to a gas phase in equilibrium with a contiguous solid or liquid phase.

418 Expansion of this phase to lower pressures en route from source to surface results in the formation

419   of a very small (< 2 volume percent) saline liquid phase that is over-represented in fluid inclusion
420   assemblages because of its wetting properties (Mernagh et al., 2020), or halite (Lecumberri-
421   Sanchez et al., 2015; Weis et al., 2012). These phase relationships are shown in Figure 9
422   with reference to the melting regime of diorite and the pressure conditions calculated here for
423   contact metamorphism (Stage 1) and the expansion of a magmatic vapour (Stage 2). Since rock
424   materials are insulators, the expansion path of a magmatic vapour through fracture arrays to the
425   surface is constrained to be irreversible and isenthalpic but may be reversible and isentropic as
426   it is released from the magma into the array (Anderson and Crerar, 1993; Barton and Toulmin,
427   1961). The isenthalpic paths indicated in Figure 9 are for the PT conditions estimated here for our
428   samples from the EESS and show a single phase low density gas phase expanding from a magma
429   complex beneath the system to low pressure towards the surface where they may intersect the liquid
430   + vapour or halite + vapour regions. The phase state projections are shown in enthalpy-pressure
431   space to demonstrate expansion paths for the EESS within the constraints of energy and mass
432   conservation (Mernagh et al., 2020). The use of temperature was omitted, because it is not an
433   extensive property of a fluid phase. For the adjacent Big Gossan Skarn (Fig. 1), Meinert et al. (1997)
434   report silicate compositions and two populations of fluid inclusion in samples taken between 2,900
435   and 3,000 m a.s.l. and therefore closer to the paleosurface than the samples reported here from the
436   EESS. The two populations of fluid inclusions reported by Meinert et al. (1997) are: (1) fluid
437   inclusions with multiple solids like halite, sylvite, chalcopyrite, hematite and anhydrite in pyroxene
438   crystals with homogenisation temperatures between 360 to 535 °C, a mean salinity of 57 wt%
439   NaCl+KCl$_{equiv}$ and no evidence of phase unmixing ('boiling') for these inclusions; (2) fluid
440   inclusions in quartz and anhydrite which are dominantly vapour-rich but also liquid-rich with an
441   average homogenisation temperature of 369 °C and a salinity of 6-8 wt% NaCl$_{equiv}$. Based on these
442   two population of fluid inclusions, Meinert et al. (1997) interpreted metamorphism and skarn
443   formation to be contiguous whereas our data, and that from calc-silicate mineralised skarns in the
444   EESS Henley et al. (2017), define the separate stages of contact metamorphism and mineralisation.
445   This is supported by the (partial) replacement of prograde Mg-silicates (e.g. olivine, diopside) by
446   anhydrite (Fig. 6). Furthermore, the widespread alteration of diopside grains evidence metasomatism
447   after diopside formation. Such subsequent, metasomatic overprint was also reported for garnets in
448   calc-silicate skarns Henley et al. (2017). The fluid inclusion data of Meinert et al. (1997) is more
449   rigorously interpreted on the basis of a low salinity, low density, high enthalpy continuum fluid
450   from which a very small amount of high salinity liquid or halite exsolved as described by Mernagh
451   et al. (2020) for the adjacent Grasberg and other copper deposits. The co-existing liquid and
452   vapour inclusions indicate trapping during phase unmixing and subsequent heat transfer from
453   wallrock to produce hypersaline inclusions as described by Mernagh et al. (2020). This approach
454   obviates the otherwise unanswered question of the source of thermal energy (> 2 kJ/kg) to sustain

455 boiling in the model proposed by Meinert et al. (1997).

### 5.2.3 Formation of anhydrite and precipitation of Cu

457 The principal Stage 2 alteration observed in sample CS1 and FM1 is the metasomatic replacement of

458 calcite ($CaCO_3$) by anhydrite ($CaSO_4$) which may be expressed as the mass balance equation (2).

459 $$CaCO_{3\,(s)} + 2SO_{2\,(g)} + 2H_{2\,(g)} \rightarrow CaSO_{4\,(s)} + H_2S_{(g)} + CO_{2\,(g)} + H_2O_{(g)} \qquad (2)$$

460 Log ($K$) for this reaction varies from 8 at 700 °C to 12.3 at 500 °C ($K$ is the equilibrium constant). The

461 reduced sulfur forms Cu-Fe-sulphide minerals from Cu and Fe transported in the general flux of

462 magmatic gas (Henley et al., 2015; Henley and Seward, 2018), the iron largely released from

463 wallrock. This alteration sequence is preserved, for instance, in the NE quadrant of Fig. 4b

464 within the transition into the Mg-rich, forsterite and diopside containing contact zone.

465 Saadatfar et al. (2020) have shown experimentally that this process is kinetically favourable

466 and is sustained by the highly connected porosity of the intergranular anhydrite that develops

467 along grain boundaries in carbonate rock material (see their Fig. 1c-d). Their experiments also

468 showed that percolation channels were maintained through the bulk rock by the anisotropic expansion

469 of calcite and the connectivity of the porous anhydrite product layer along these grain boundaries. In

470 the stressed environment of an active volcanic system tensile fractures are likely to continuously

471 reopen. Because fractures therefore remain permeable, the conversion rate of carbonate to anhydrite

472 through nucleation and growth of anhydrite crystals is only limited by the rates of ingress and

473 egress of reactant and product gases at the reaction front of each calcite grain. The deposition of

474 economic amounts of Cu-Fe-sulphides within the altered and metasomatised regions of CS1 and, with

475 anhydrite in FM1, provides evidence of the pervasive flow of metal-bearing, magma-derived fluid in

476 Stage 2. It is the *in situ* generation of $H_2S_{(g)}$ that drives economic copper deposition (as bornite)

477 due to its very low solubility as is observed in sample FM1 and throughout the system. Bornite

478 deposition may be represented by the synoptic mass-balance reaction equation,

479 $$5CuCl_{(g)} + FeCl_{(g)} + 4H_2S_{(g)} = Cu_5FeS_4 + 6HCl_{(g)} + H_{2(g)} \qquad (3)$$
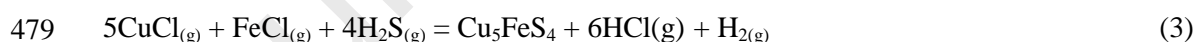
480 for which log ($K$) at 700 °C is $4\times10^{54}$ and $3.8\times10^{63}$ at 600 °C. The reaction is written using the

481 dominant Cu and Fe species determined elsewhere for magmatic arc volcanic gases (Henley and

482 Seward, 2018). The speciation of metals in high temperature gas mixtures is complex so that other Fe

483 and Cu species occur at lower concentrations and in an equilibrium model any one of them may be

484 used to express solubility reactions but the speciation shown here expresses the highest contribution

485 to bornite solubility noting that at much higher initial sulfur concentrations the species $Cu_2S_{(g)}$ may

486 become important. Although the EESS is of economic importance of its copper content, the

487 sulphur anomaly that the deposit represents is compelling in terms of the volume of rock that

488 experiences the addition of sulphur. Extensive drilling data (kindly provided by P.T. Freeport

489 Indonesia) show that the amount of forsterite-dominated skarn in the EESS is ~1,485 Mt.

14

Considering the abundance of anhydrite observed in the sample FM1, the amount of anhydrite within the forsterite-dominated skarns of the EESS is ~1,100 Mt (Table S2 in the supplementary information). The implication of reaction (2) is that metasomatism of the carbonate sediment formed this amount of anhydrite and required a total flux of ~1,050 Mt of $SO_{2(g)}$. Hughes et al. (2016) reported $SO_{2(g)}$ flux data for arc volcanic gases from modern volcanoes as between ~73 to 21,000 tonnes per day with a median $SO_{2(g)}$ flux of 735 tonnes per day. Using this median $SO_{2(g)}$ flux, the lifetime of the degassing EESS system could have been around 3,900 years (Table S2 in the supplementary information). In order to sustain such flux during Stage 2 at the relatively shallow paleo-depth of the system, the fracture array would necessarily have been open to the surface and sustained a range of shallow hydrothermal phenomena such as fumaroles and solfatara.

## 5.3 Stage 3: Retrograde hydration

Retrograde alteration (Stage 3) occurred when the magmatic system waned resulting in a decrease in temperature and magmatic vapour flux compared to the skarn mineralisation stage (Stage 2). $H_2O$-rich fluids trapped during Stage 2 or flooding from the surrounding country rock into the mineralised skarns (e.g., Fig. 15 in King et al. (2018)) caused retrograde hydration. The lack of retrograde carbonation indicates relatively low $X_{CO_{2(g)}}$ in the ambient fluid (forsterite and diopside are not carbonated, but partially hydrated to serpentine (Fig. 3 and 5a)). Anhydrite is preserved because the temperatures were relatively high at the low pressures of serpentinization (e.g. Blounot and Dickson (1969); Fig. 16 in King et al. (2018)).

# 6 Conclusions

We have here described the development of mineralised Mg-silicate skarns in the East Ertsberg Skarn System from contact metamorphism of carbonate-rich sediments by the Ertsberg Intrusion (Stage 1 at 2.7-2.9 Ma), through subsequent high temperature alteration by a flux of magmatic gas (Stage 2) to subsequent overprinting by retrograde, hydrothermal alteration (Stage 3). During contact metamorphism (Stage 1), temperatures have here been shown through mineral chemistry and thermochemical analysis to have reached 750 ± 50 ℃ at the sample depth where lithostatic pressure was 51 ± 5 MPa. In Stage 2, the flux of magmatic gas from the Ertsberg Intrusion resulted in the conversion of members of the New Guinea Limestone Group to mineralised skarns and replacement bodies up to 1 km from the igneous contact and a paleodepth range from about 0.5 to over 2.5 km (Fig. 1d). Typical porphyry copper alteration and mineralisation occurs in the Ertsberg intrusion but magmatic gas expansion was mainly channeled through the embrittled, contact-metamorphosed marble sequence. The combination of continuing tectonic and thermal stress with the generation of porous anhydrite maintained the high permeability of this sequence and sustains bulk sulphate metasomatism and Cu mineralisation within >2,600 Mt of exoskarns. About 60 wt% of this exoskarn

524 was converted from a carbonate-rich assemblage to one dominated by forsterite, anhydrite and
525 sulphide minerals. Geologic data show that these processes operated to within one kilometer of the
526 paleo-surface and required the throughput of at least 1,050 Mt of $SO_{2\,(g)}$. The hydrodynamic and
527 chemical environment responsible for mineralisation within the EESS is similar to those responsible
528 for the formation of sub-volcanic porphyry copper systems (Henley and McNabb, 1978;
529 Jochum et al., 2012; Lecumberri-Sanchez et al., 2015) where a magmatic fluid phase
530 expands through the upper crust to form a gas-dominated hydrodynamic plume that vents to the
531 surface. Most porphyry copper systems are hosted by intrusive and related volcanic rocks but in the
532 EESS much of the flux was focussed through and mineralised the contact metamorphosed and
533 embrittled carbonate sequence, while dispersion through the upper part of the Ertsberg intrusion
534 formed porphyry copper and endoskarn-style alteration and mineralisation. The context for skarn
535 alteration and mineralisation provided here is therefore compatible with the occurrence of low grade
536 *porphyry copper* style alteration and mineralisation in the upper part of the Ertsberg intrusion (Leys
537 et al., 2012). In other words it is a consequence of reactive mass transport in a magmatic vapour
538 plume (Henley and McNabb, 1978; Henley et al., 2015; Weis, 2015; Weis et al.,
539 2012) fluxing from an intrusive source regime through fractured reactive (meta-) sedimentary rock
540 to surface.

## 7    Acknowledgments

## 8    References

549 Anderson, G. M., and Crerar, D. A., 1993, Thermodynamics in geochemistry: The equilibrium model,
550     Oxford University Press on Demand.
551 Baline, L. M., 2007, Hydrothermal Fluids and Cu-Au Mineralization of the Deep Grasberg Porphyry
552     Deposit, Papua, Indonesia [Thesis: University of Texas, Austin, 287 p.
553 Barton, P. B., and Toulmin, P., 1961, Some mechanisms for cooling hydrothermal fluids: US
554     Geological Survey Professional Paper, v. 424, p. 348-352.
555 Blounot, C., and Dickson, F., 1969, The solubility of anhydrite (CaSO4) in NaCl-H2O from 100 to
556     450 C and 1 to 1000 bars: Geochimica et Cosmochimica Acta, v. 33, no. 2, p. 227-245.
557 Bucher-Nurminen, K., 1982, Mechanism of Mineral Reactions Inferred from Textures of Impure
558     Dolomitic Marbles from East Greenland: Journal of Petrology, v. 23, no. 3, p. 325-343.
559 Bucher, K., and Grapes, R., 2011, Metamorphism of Dolomites and Limestones, Petrogenesis of
560     Metamorphic Rocks, Springer, p. 225-255.
561 Cloos, M., and Sapiie, B., 2013, Porphyry copper deposits: strike-slip faulting and throttling cupolas:
562     International Geology Review, v. 55, no. 1, p. 43-65.
563 Connolly, J. A. D., 2009, The geodynamic equation of state: What and how: Geochemistry

564   Geophysics Geosystems, v. 10, no. 10, p. 1525-2027.

565 Cox, S. F., 2010, The application of failure mode diagrams for exploring the roles of fluid pressure
566   and stress states in controlling styles of fracture-controlled permeability enhancement in
567   faults and shear zones: Geofluids, v. 10, no. 1-2, p. 217-233.

568 Diener, J. F. A., and Powell, R., 2012, Revised activity-composition models for clinopyroxene and
569   amphibole: Journal of Metamorphic Geology, v. 30, no. 2, p. 131-142.

570 Driesner, T., 2007, The system $H_2O$–NaCl. Part II: Correlations for molar volume, enthalpy, and
571   isobaric heat capacity from 0 to 1000° C, 0 to 5000bar, and 0 to 1 X NaCl: Geochimica et
572   Cosmochimica Acta, v. 71, no. 20, p. 4902-4919.

573 Einaudi, M. T., and Burt, D. M., 1982, A Special Issue Devoted to Skarn Deposits - Introduction -
574   Terminology, Classification, and Composition of Skarn Deposits: Economic Geology, v. 77,
575   no. 4, p. 745-754.

576 Fuhrman, M., and Lindsley, D., 1988, Feldspar minerals: American Mineralogist, v. 73, p. 201-215.

577 Fulignati, P., Kamenetsky, V. S., Marianelli, P., Sbrana, A., and Mernagh, T. P., 2001, Melt inclusion
578   record of immiscibility between silicate, hydrosaline, and carbonate melts: Applications to
579   skarn genesis at Mount Vesuvius: Geology, v. 29, no. 11, p. 1043-1046.

580 Gandler, L., 2006, Calc-silicate alteration and Cu-Au mineralization of the Deep MLZ skarn; Ertsberg
581   District, Papua, Indonesia [Master Thesis Master]: University of Texas, Austin.

582 Gibbins, S. L., 2006, The Magmatic and Hydrothermal Evolution of the Ertsberg Intrusion in the
583   Gunung Bijih (Ertsberg) Mining District, West Papua, Indonesia [PhD Thesis PhD]:
584   University of Arizona, 384 p.

585 Harrison, J. S., 1999, Hydrothermal alteration and fluid evolution of the Grasberg porphyry Cu-Au
586   deposit, Irian Jaya, Indonesia [Master Thesis Master]: University of Texas, Austin, 205 p.

587 Henley, R., and McNabb, A., 1978, Magmatic vapor plumes and ground-water interaction in porphyry
588   copper emplacement: Economic Geology, v. 73, no. 1, p. 1-20.

589 Henley, R. W., Brink, F. J., King, P. L., Leys, C., Ganguly, J., Mernagh, T., Middleton, J., Renggli, C.
590   J., Sieber, M., Troitzsch, U., and Turner, M., 2017, High temperature gas-solid reactions in
591   calc-silicate Cu-Au skarn formation; Ertsberg, Papua Province, Indonesia: Contributions to
592   Mineralogy and Petrology, v. 172, no. 11-12, p. 106.

593 Henley, R. W., and Hughes, G. O., 2016, SO2 flux and the thermal power of volcanic eruptions:
594   Journal of Volcanology and Geothermal Research, v. 324, p. 190-199.

595 Henley, R. W., King, P. L., Wykes, J. L., Renggli, C. J., Brink, F. J., Clark, D. A., and Troitzsch, U.,
596   2015, Porphyry copper deposit formation by sub-volcanic sulphur dioxide flux and
597   chemisorption: Nature Geoscience, v. 8, no. 3, p. 210-215.

598 Henley, R. W., and Seward, T. M., 2018, Gas-Solid Reactions in Arc Volcanoes: Ancient and
599   Modern: High Temperature Gas-Solid Reactions in Earth and Planetary Processes, v. 84, no.
600   1, p. 309-349.

601 Holland, T., and Powell, R., 1991, A compensated-Redlich-Kwong (CORK) equation for volumes
602   and fugacities of CO2 and H2O in the range 1 bar to 50 kbar and 100–1600C: Contributions
603   to Mineralogy and Petrology, v. 109, no. 2, p. 265-273.

604 -, 2003, Activity–composition relations for phases in petrological calculations: an asymmetric
605   multicomponent formulation: Contributions to Mineralogy and Petrology, v. 145, no. 4, p.
606   492-501.

607 Holland, T. J. B., and Powell, R., 1998, An internally consistent thermodynamic data set for phases of
608   petrological interest: Journal of Metamorphic Geology, v. 16, no. 3, p. 309-343.

609 -, 2011, An improved and extended internally consistent thermodynamic dataset for phases of
610   petrological interest, involving a new equation of state for solids: Journal of Metamorphic
611   Geology, v. 29, no. 3, p. 333-383.

612 Holtz, F., Becker, A., Freise, M., and Johannes, W., 2001, The water-undersaturated and dry Qz-Ab-
613   Or system revisited. Experimental results at very low water activities and geological
614   implications: Contributions to Mineralogy and Petrology, v. 141, no. 3, p. 347-357.

615 Hughes, J. M., Harlov, D., Kelly, S. R., Rakovan, J., and Wilke, M., 2016, Solid solution in the apatite
616   OH-Cl binary system: Compositional dependence of solid-solution mechanisms in calcium
617   phosphate apatites along the Cl-OH binary: American Mineralogist, v. 101, no. 8, p. 1783-
618   1791.

Jochum, K. P., Scholz, D., Stoll, B., Weis, U., Wilson, S. A., Yang, Q., Schwalb, A., Börner, N., Jacob, D. E., and Andreae, M. O., 2012, Accurate trace element analysis of speleothems and biogenic calcium carbonates by LA-ICP-MS: Chemical Geology, v. 318, p. 31-44.

King, P. L., Wheeler, V. M., Renggli, C. J., Palm, A. B., Wilson, S. A., Harrison, A. L., Morgan, B., Nekvasil, H., Troitzsch, U., Mernagh, T., Yue, L., Bayon, A., DiFrancesco, N. J., Baile, R., Kreider, P., and Lipinski, W., 2018, Gas-Solid Reactions: Theory, Experiments and Case Studies Relevant to Earth and Planetary Processes: High Temperature Gas-Solid Reactions in Earth and Planetary Processes, v. 84, no. 1, p. 1-56.

Kullerud, G., Yund, A., and Moh, G., 1969, Phase relation in the Cu-Fe-S, Cu-Ni-S and Fe-Ni-S System: Carnegie Institute of Washington Year Book, v. 15, p. 323-343.

Kyle, J. R., Gandler, L., Mertig, H., Rubin, J., and Ledvina, M., 2014, Stratigraphic Inheritance Controls of Skarn-hosted Metal Concentrations: Ore controls for Ertsberg-Grasberg District Cu-Au skarns, Papua, Indonesia: Acta Geologica Sinica (English Edition), v. 88, no. s2, p. 529-531.

Lecumberri-Sanchez, P., Steele-MacInnis, M., Weis, P., Driesner, T., and Bodnar, R. J., 2015, Salt precipitation in magmatic-hydrothermal systems associated with upper crustal plutons: Geology, v. 43, no. 12, p. 1063-1066.

Leys, C. A., Cloos, M., New, B. T., and MacDonald, G. D., 2012, Copper-gold±molybdenum deposits of the Ertsberg-Grasberg District Papua, Indonesia: Society of Economic Geologists, Special Publication, v. 16, p. 215-235.

Macdonald, G. D., and Arnold, L. C., 1994, Geological and Geochemical Zoning of the Grasberg Igneous Complex, Irian-Jaya, Indonesia: Journal of Geochemical Exploration, v. 50, no. 1-3, p. 143-178.

Matthews, S. J., Marquillas, R. A., Kemp, A. J., Grange, F. K., and Gardeweg, M. C., 1996, Active skarn formation beneath Lascar Volcano, northern Chile: a petrographic and geochemical study of xenoliths in eruption products: Journal of Metamorphic Geology, v. 14, no. 4, p. 509-530.

McMahon, T. P., 1994, Pliocene Intrusions in the Gunung Bijih (Ertsberg) Mining District, Irian Jaya, Indonesia: Petrography and Mineral Chemistry: International Geology Review, v. 36, no. 9, p. 820-849.

Meinert, L. D., Dipple, G. M., and Nicolescu, S., 2005, World skarn deposits: Economic Geology v. 100th Anniversary Volume, p. 299-336.

Meinert, L. D., Hefton, K. K., Mayes, D., and Tasiran, I., 1997, Geology, zonation, and fluid evolution of the big Gossan Cu-Au skarn deposit, Ertsberg district: Irian Jaya: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 92, no. 5, p. 509-534.

Mernagh, T., Leys, C., and Henley, R. W., 2020, Fluid inclusion systematics in porphyry copper deposits: The super-giant Grasberg deposit, Indonesia, as a case study: Ore Geology Reviews, v. 123.

Mertig, H. J., 1995, Geology and Ore Formation of the Dom Copper Skarn Deposit, Ertsberg (Gunung Bijih) District, Irian Jaya, IndonesiaMaster]: University of Texas.

Mertig, H. J., Rubin, J. N., and Kyle, J. R., 1994, Skarn Cu-Au Orebodies of the Gunung-Bijih (Ertsberg) District, Irian-Jaya, Indonesia: Journal of Geochemical Exploration, v. 50, no. 1-3, p. 179-202.

Paterson, J. T., and Cloos, M., 2005, Grasberg porphyry Cu–Au deposit, Papua, Indonesia: 1. Magmatic history, South Australia, PGC Publishing, Super porphyry copper and gold deposits: A global perspective, 313-330 p.:

Pirajno, F., 2013, Effects of Metasomatism on Mineral Systems and Their Host Rocks: Alkali Metasomatism, Skarns, Greisens, Tourmalinites, Rodingites, Black-Wall Alteration and Listvenites, Metasomatism and the Chemical Transformation of Rock: The Role of Fluids in Terrestrial and Extraterrestrial Processes: Berlin, Heidelberg, Springer Berlin Heidelberg, p. 203-251.

-, 2018, Halogens in hydrothermal fluids and their role in the formation and evolution of hydrothermal mineral systems, The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes, Springer, p. 759-804.

Pollard, P. J., and Taylor, R. G., 2002, Paragenesis of the Grasberg Cu-Au deposit, Irian Jaya,

674　　　　　Indonesia: results from logging section 13: Mineralium Deposita, v. 37, no. 1, p. 117-136.

675　Proyer, A., Mposkos, E., Bazicitis, I., and Hoinkes, G., 2008, Tracing high-pressure metamorphism in
676　　　　　marbles: Phase relations in high-grade aluminous calcite-dolomite marbles from the Greek
677　　　　　Rhodope massif in the system CaO-MgO-Al2O3-SiO2-CO2 and indications of prior
678　　　　　aragonite: Lithos, v. 104, no. 1-4, p. 119-130.

679　Saadatfar, M., Brink, F., Latham, S., King, P., Middleton, J., Troitzsch, U., Turner, M., and Henley,
680　　　　　R. W., 2020, High resolution 3D mapping of grain kinematics during high temperature
681　　　　　sequestration of SO2 from flue gas by carbonate aggregates: Sci Rep, v. 10, no. 1, p. 2201.

682　Satish-Kumar, M., Wada, H., Santosh, M., and Yoshida, M., 2001, Fluid-rock history of granulite
683　　　　　facies humite-marbles from Ambasamudram, southern India: Journal of Metamorphic
684　　　　　Geology, v. 19, no. 4, p. 395-410.

685　Skippen, G., 1974, An experimental model for low pressure metamorphism of siliceous dolomitic
686　　　　　marble: American Journal of Science, v. 274, no. 5, p. 487-509.

687　Thu, Y. K., and Enami, M., 2018, Evolution of metamorphic fluid recorded in granulite facies
688　　　　　metacarbonate rocks from the middle segment of the Mogok metamorphic belt in central
689　　　　　Myanmar: Journal of Metamorphic Geology, v. 36, no. 7, p. 905-931.

690　Turner, F. J., 1981, Metamorphic petrology: Mineralogical, field, and tectonic aspects, Washington,
691　　　　　New York, and London (McGraw Hill), McGraw-Hill Companies.

692　Wafforn, S., 2017, Geo-and Thermochronology of the Ertsberg-Grasberg Cu-Au Mining District,
693　　　　　West New Guinea, IndonesiaPhD]: University of Texas.

694　Wafforn, S., Seman, S., Kyle, J. R., Stockli, D., Leys, C., Sonbait, D., and Cloos, M., 2018, Andradite
695　　　　　garnet U-Pb geochronology of the big Gossan skarn, Ertsberg-Grasberg mining district,
696　　　　　Indonesia: Economic Geology, v. 113, no. 3, p. 769-778.

697　Warren, J. K., 2016, Magma-Evaporite-Hydrothermal Metal Associations, Evaporites: Switzerland,
698　　　　　Springer, Cham, p. 1591-1657.

699　Weis, P., 2015, The dynamic interplay between saline fluid flow and rock permeability in magmatic-
700　　　　　hydrothermal systems: Geofluids, v. 15, no. 1-2, p. 350-371.

701　Weis, P., Dreisner, T., and Heinrich, C. A., 2012, Porphyry-copper ore shells form at stable pressure-
702　　　　　temperature fronts within dynamic fluid plumes: Science, v. 338, p. 1613-1616.

703　Wheller, C. J., and Powell, R., 2014, A new thermodynamic model for sapphirine: calculated phase
704　　　　　equilibria in K2O-FeO-MgO-Al2O3-SiO2-H2O-TiO2-Fe2O3: Journal of Metamorphic
705　　　　　Geology, v. 32, no. 3, p. 287-299.

706　White, R. W., Powell, R., and Clarke, G. L., 2002, The interpretation of reaction textures in Fe-rich
707　　　　　metapelitic granulites of the Musgrave Block, central Australia: constraints from mineral
708　　　　　equilibria calculations in the system K2O-FeO-MgO-Al2O3-SiO2-H2O-TiO2-Fe2O3:
709　　　　　Journal of Metamorphic Geology, v. 20, no. 1, p. 41-55.

710　Yund, R. A., and Kullerud, G., 1966, Thermal stability of assemblages in the Cu—Fe—S system:
711　　　　　Journal of Petrology, v. 7, no. 3, p. 454-488.

712　Zhu, Q. Q., Xie, G. Q., Mao, J. W., Li, W., Li, Y. H., Wang, J., and Zhang, P., 2015, Mineralogical
713　　　　　and sulfur isotopic evidence for the incursion of evaporites in the Jinshandian skarn Fe
714　　　　　deposit, Edong district, Eastern China: Journal of Asian Earth Sciences, v. 113, p. 1253-1267.

715

716　**Figure Captions**

717　**Fig. 1** (a) Ertsberg district geological map modified after Henley et al. (2017), (b) EESS geological

718　map at a 1.7 km elevation plane, and (c) Cross-section of the Ertsberg East Skarn System provided

719　by PT Freeport Indonesia; (b) and (c) show the drill hole TE06-24 from which the investigated

720　samples (CS1 and FM1) were taken. The samples (CS1 and FM1) come from the Waripi Formation

721　(Tw) which is the lowest formation within the New Guinea Limestone Group. (d) Schematic

722　projection of the relative position and scale of alteration and mineralisation for the EESS, the

723  slightly older Grasberg porphyry copper system (and its open pit mine outline), and other district
724  skarn deposits, modified after Leys et al. (2012). Note that this figure shows the location and extent
725  of mineralisation rather than geological data.

726  **Fig. 2** Si-Ca-Mg+Fe ternary diagram comparing the reconstructed bulk composition of the
727  investigated samples, CS1 (circles) and FM1 (triangle), to the seven stratigraphic units of
728  unmetamorphosed and unaltered sediments of the Waripi Formation (squares) studied by Gandler
729  (2006) and to ICP-AES bulk rock data of exoskarns from the Waripi Formation (data kindly
730  provided from Freeport Indonesia). The plotted exoskarns (diamonds) were collected within a
731  distance of 15 to 150 m to CS1 and FM1. The reconstructed bulk composition of sample FM1
732  correlates reasonably well to limestones and sandy dolostones of the unmetamorphosed Waripi
733  Formation. Like the Waripi-exoskarns, CS1-lower-contact and CS1-Mg-rich-silicate have higher
734  Mg+Fe and lower Si compared to the unaltered sediments.

735  **Fig. 3** Sample FM1: (a, b) ™QEMSCAN maps visualising the phase distribution of anhydrite and
736  forsterite dominated sample FM1. (c) BSE-image of prograde forsterite with phlogopite inclusions
737  and retrograde hydration to serpentine + magnetite at the rim. Abbreviations are: anh: anhydrite;
738  phl: phlogopite; mt2: magnetite likely formed in Stage 2 (associated with anhydrite); mt3:
739  magnetite likely formed in Stage 3 associated with serpentinization of olivine.

740  **Fig. 4** Sample CS1: (a) photography of sample CS1 showing the stratigraphic upper calc-silicate
741  studied by Henley et al. (2017) and the lower Mg-rich silicate investigated in this study. A
742  grossular-diopside assemblage formed during Stage 1 contact metamorphism in the calc-silicate
743  altered into an andradite-anorthite assemblage with anhydrite, chalcopyrite and anorthite selvedges
744  during skarn mineralisation (for details see Henley et al. (2017)). The assemblage change through
745  diopside-anhydrite (upper contact) and phlogopite-pargasite (lower contact) into the Mg-silicate
746  containing mainly pargasite, forsterite and diopside. The mineralogy of the contact zone and the
747  Mg-silicate is shown in (b) by the ™QEMSCAN map. In the contact zone and in the Mg-rich
748  silicate, diopside, forsterite, phlogopite, pargasie and Al-spinel (plus calcite) are formed during
749  contact metamorphic. Anhydrite and Fe-Cu-sulphides evidence the input of a magmatic, $SO_2$-rich
750  gas during Stage (2) alteration. Serpentine (and magnetite) are formed during retrograde hydration
751  (Stage 3). (c) Shows higher resolution detail for part of the altered Mg-silicate-anhydrite-sulphide
752  assemblage in order to define timing relations for mineral phases.

753  **Fig. 5** Sample CS1: (a) detailed ™QEMSCAN map visualising the mineral assemblage and
754  textures discussed in the text for the diopside-anhydrite rich, upper part of the contact zone, for the
755  pargasite-phlogopite rich, lower part of the contact zone and the pargasite-forsterite rich Mg-
756  silicate. The location of the displayed detailed ™QEMSCAN is indicated in the photography of the
757  sample (see Fig. 4). (b, c) Highlighting the textures and phase relations, areas of the (b) pargasite-

758    phlogopite contact zone and (c) from the pargasite-forsterite dominated Mg-silicate.
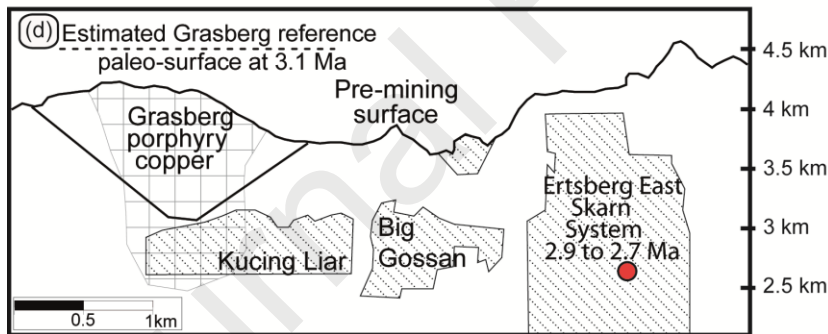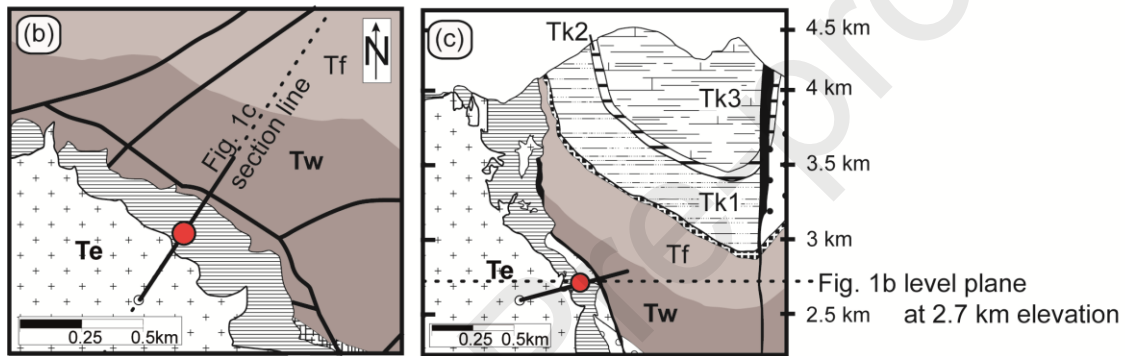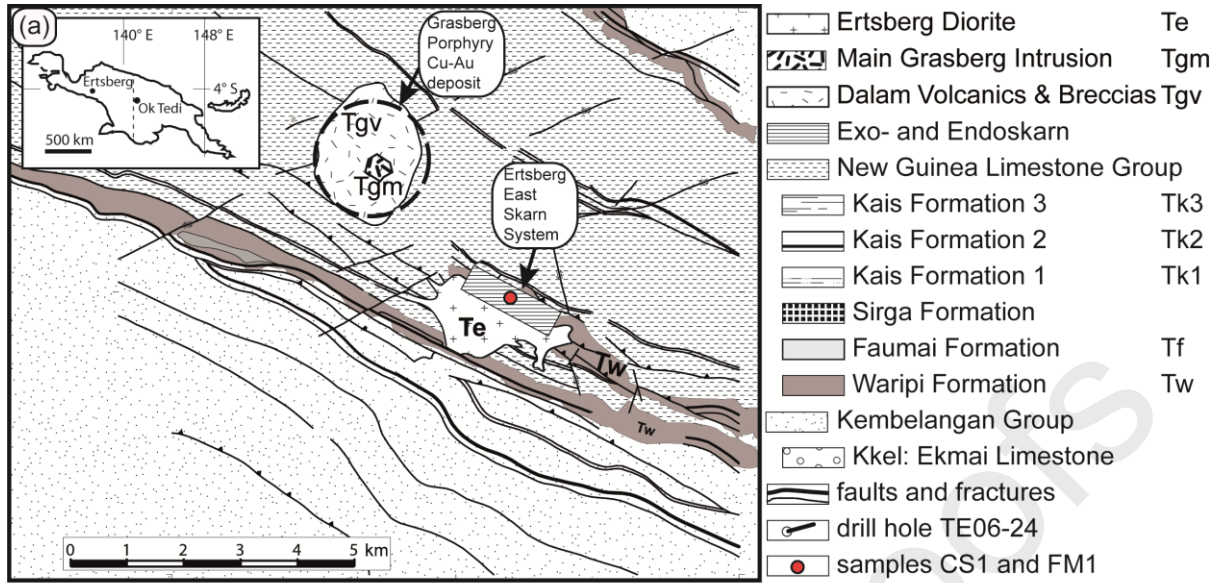
759    **Fig. 6** BSE-image of diopside grain evidencing significant variations in respect to the Mg# of

760    diopside (numbers refer to Mg# of diopside). The irregular shape of the diopside grain and the

761    compositional variation within the diopside grain indicate partial alteration of diopside during Stage
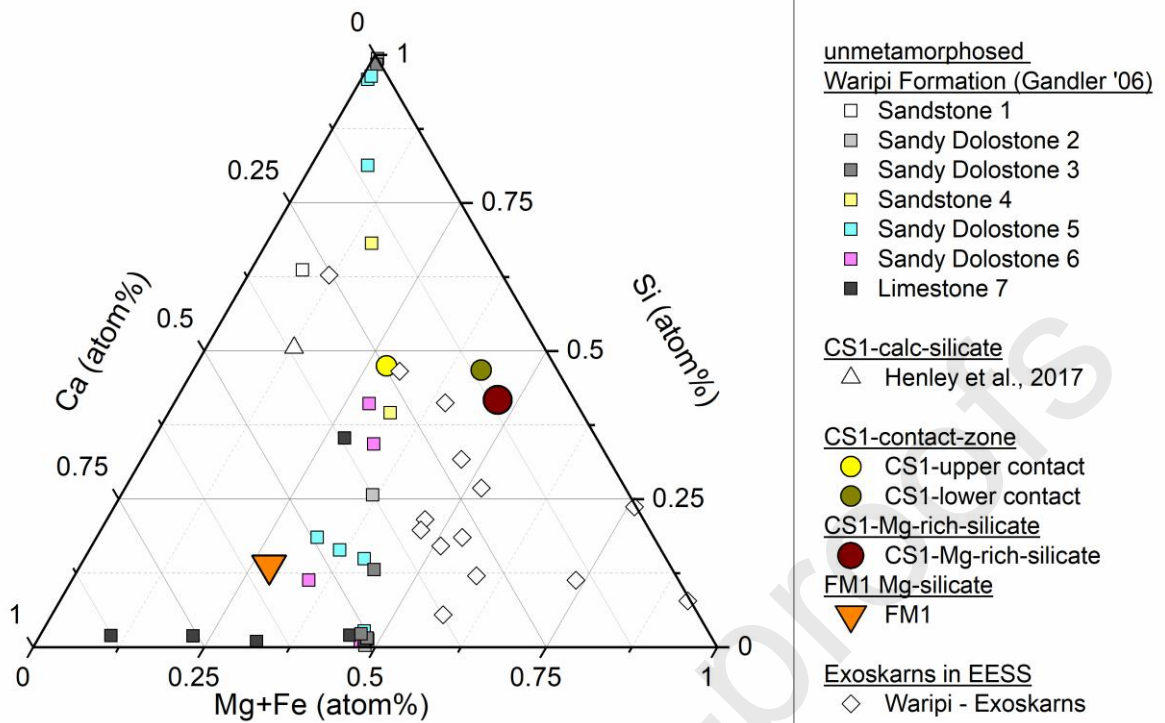
762    2 sulphate metasomatism.

763    **Fig. 7** (a-d) BSE-images of Cu-Fe-sulphides associated with anhydrite from CS1; (e) ternary Cu-

764    Fe-S diagram at 700 °C after Kullerud et al. (1969); Yund and Kullerud (1966) showing

765    compositional variability of Cu-Fe-sulphides. Some measurements spots are indicated in the BSE-

766    images (c-d). Abbreviations and symbols: Anh: anhydrite; Bor: bornite (circle); Cal: Chalcocite

767    (rectangle); Cp: Chalcopyrite; Fe: iron; Po: pyrrhotite; Phl: phlogopite; $S_L$: S-bearing liquid

768    **Fig. 8** The main phase relations of the isobaric temperature-$X_{CO_2}^{fluid}$ pseudosections modelled at 51

769    MPa for (a) the Mg-rich part of CS1 and (b) for sample FM1 are shown. The model assumes that

770    the system is saturated with a $CO_2$-$H_2O$ fluid. Recalculated bulk rock compositions, used in the

771    modelling, are reported in Table 1. Temperature-$X_{CO_2}^{fluid}$ relations discussed in greater detail in the

772    text are highlighted. Coloured solid lines refer to mineral-out reactions with increasing temperature.

773    [1] Cpx Sp cAmph mont ak kls; [2] Cpx Sp cAmph mont ne kls; [3] Cpx Bi cAmph Sp mont kls;

774    [4] Carb Cpx Sp cAmph kls; [5] Carb Chl Bi Cpx cAmph naph; [6] Carb Chl Bi Cpx cAmph nap;

775    [7] Chl Bi Carb Cpx nap; [8] Chl Bi Carb Cpx oAmph naph; [9] Chl Bi Carb Cpx naph dol; [10]

776    Chl Bi Cpx cAmph naph dol; [11] Chl Bi Cpx cAmph dol; [12] Carb Bi Sp Ol mont wu; [13] Carb

777    Bi Ol Sp vsv; [14] Ol Carb Sp ak kls Abbreviations: ak: akermanite; Bi: Biotite; cAmph: clino

778    Amphibole; Carb: Carbonate; Chl: Chlorite; Cpx: Clinopyroxene; dol: dolomite; kls: kalsinite;

779    mont: monticellite; naph: Na-phlogopite: ne: nepheline; Sp: Spinel; wu: wustite; vsv: vesuvianite

780    (capital letters are used to indicate solid solutions and small letters are used for endmember

781    compositions).

782    **Fig. 9** Isothermic projection of the phase relations and density isopleths for the NaCl-$H_2O$ system

783    relative to the melting regime of diorite (Holtz et al., 2001). The phase relationships are compiled

784    from the data of Driesner (2007). The isenthaltic expansion path of a low density, magmatic gas

785    during Stage 2 (skarn formation and alteration) is shown for the PT conditions estimated here for

786    our samples from the EESS. Towards the (paleo-) surface the expanding vapour may intersect the

787    vapour + liquid or vapour + halite regions.

788

790



791

(a)

Anhydrite-
chalcopyrite
and
anorthite
selvedge

Andradite-
anorthite
assemblage

Grossular-
diopside
assemblage

CS1 -
calc -
silicate

CS1 -
contact
zone

Fig.5

Fig.4b

CS1 -
Mg-rich
silicate

10 mm

Legend: Figures 4b and c
Diopside          Anhydrite
Phlogopite        Bornite
Forsterite        Pargasite
Al-spinel         Serpentine
Garmet    } only present in Calc-silicate
Anorthite

(b)

Fig.4c

Fig.5

CS1 -
calc -
silicate

CS1 -
upper
contact
zone

CS1 -
lower
contact
zone

CS1 -
Mg-rich-
silicate

1 mm

(c)

0.5 mm

792

24

793



794

(a) Anh CuFe-Sulphide Cal Phl Phl 100µm

(b) Anh Anh CuFe-Sulphide Phl 50µm

(c) 50µm

(d) Zn-Covellite 50µm

(e) S (wt%) 0.50 0.50
S_L +Cp +Bor Fe +Po +Bor
0.75 Bor 0.25
Cal Cu+Fe+Bor
1.00 0.00
Cu 0.00 0.25 0.50 Fe

● Bornite
★ Intermediate Solid Solution
□ Chalcocite

795

(a) CS1-Mg-rich-silicate 51 MPa

+ Olivine

(b) FM1 51 MPa

796

| Carbonate | Pargasite | Phlogopite | Spinel | Diopside | Olivine |



797

simplified sketch of fluid-rock interaction detailed in this research
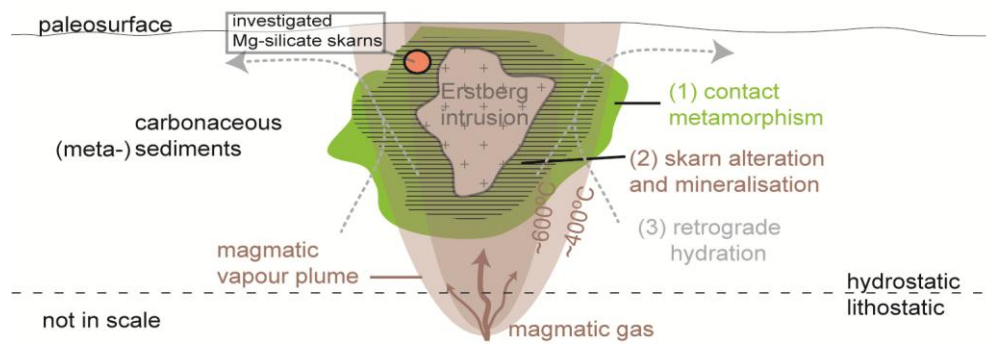


- 798
- 799 Contact metamorphism at 51±5 MPa and 750 ± 50 °C formed forsterite + calcite + phlogopite
- 800 some diopside and spinel and rare pargasite
- 801 A magmatic vapor plume fluxing from an intrusive source regime through fractured
- 802 (meta-) sedimentary rock to surface converted carbonates into anhydrite and caused
- 803 precipitation of Cu-Fe-sulphites (e.g. bornite) and pyrite
- 804 Formation of Mg-rich silicate skarn at East Ertsberg Skarn System required a flux of
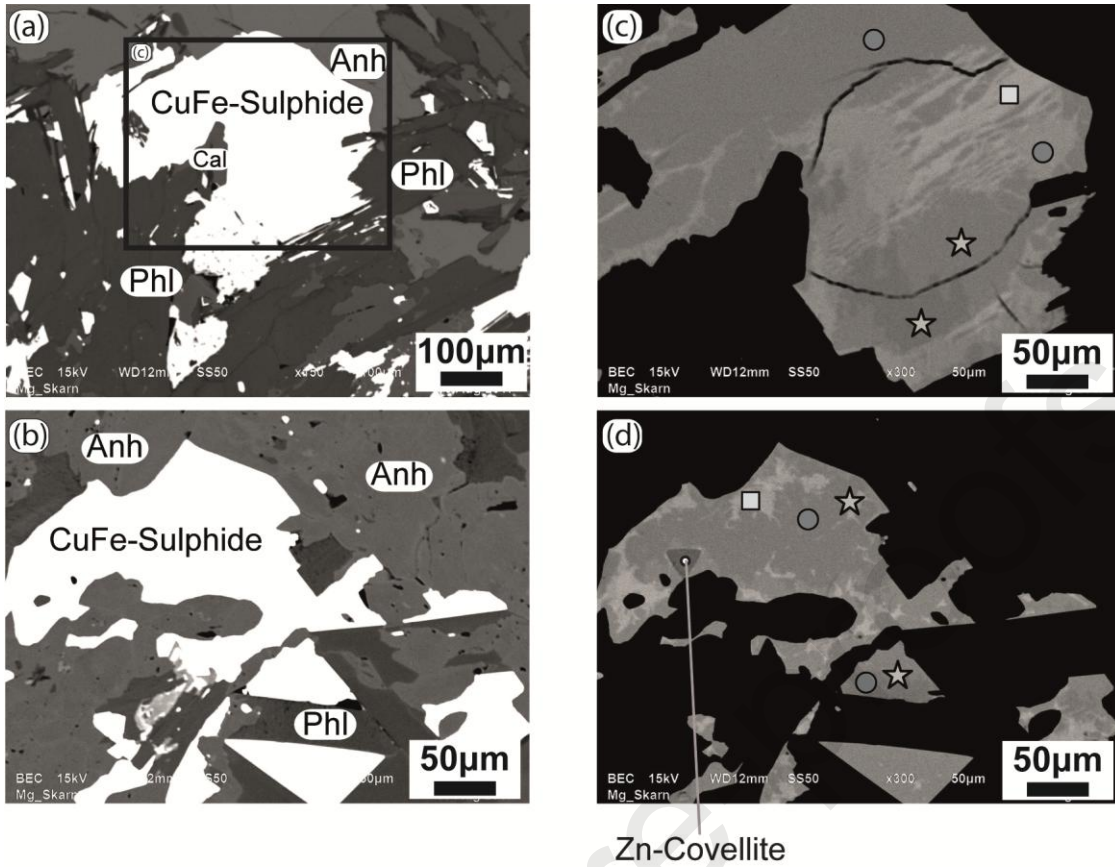- 805 ~1,050 Mt $SO_2$ and may lasted for ~3,900 years.

806

807

808

809 **Table 1.** Phase abundances constrained in ™QEMSCAN maps and major element composition of
810 mineral phases per FE-EPMA of the upper and lower contact of sample CS1, the Mg-silicate part of
811 sample CS1 and sample FM1.

| Sample | Lithology | mineral phases | Abundances per QEMSCAN Area% | median composition | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $SiO_2$ wt% | $TiO_2$ wt% | $Al_2O_3$ wt% | FeO wt% | MnO wt% | Mg wt% |
| CS1 | calc-silicate [1] | bulk rock | | 42.83 | | 17.6 | 6.77 | | 3. |
| CS1 | CS1 - upper contact | Diopside | 80.0 | 48.2 | <d.l. | 2.7 | 1.8 | <d.l. | 16 |
| | | Phlogopite | 11.7 | 38.6 | 0.3 | 18.9 | 4.1 | <d.l. | 22 |
| | | Pargasite | 6.0 | 39.5 | <d.l. | 15.7 | 6.2 | <d.l. | 17 |
| | | Anhydrite | 1.9 | 0.1 | <d.l. | <d.l. | <d.l. | <d.l. | 0. |
| | | Al-spinel | 0.1 | 0.1 | <d.l. | 62.3 | 14.4 | <d.l. | 19 |
| | | Garnet | 0.1 | | | | | | nA |
| | | Bornite | 0.1 | | | | | | nA |
| | | Cr-spinel | 0.01 | | | | | | nA |
| | | **Recalulated volatile free bulk rock** | | **48.9** | | **5.7** | **2.5** | | **17** |
| CS1 | CS1 - lower contact | Phlogopite | 53.7 | 37.3 | <d.l. | 16.8 | 4.1 | <d.l. | 23 |
| | | Pargasite | 22.2 | 39.5 | <d.l. | 15.7 | 6.2 | <d.l. | 17 |
| | | Diopside | 16.2 | 48.2 | <d.l. | 2.7 | 1.8 | <d.l. | 16 |

| | | Mineral | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Al-Spinel | 3.7 | 0.1 | <d.l. | 62.3 | 14.4 | <d.l. | 19 |
| | | Anhydrite | 2.7 | 0.1 | <d.l. | <d.l. | <d.l. | <d.l. | 0. |
| | | Bornite | 0.6 | | | | | | |
| | | Cr-spinel | 0.5 | | | | | | nA |
| | | Hematite | 0.3 | | | | | | nA |
| | | Magnetite | 0.1 | | | | | | nA |
| | | Olivine | 0.1 | | | | | | nA |
| | | Serpentine | 0.03 | | | | | | nA |
| | | Garnet | 0.01 | | | | | | nA |
| | | **Recalulated volatile free bulk rock** | | **40.6** | | **16.9** | **4.9** | | **21** |
| CS1 | CS1 - Mg-rich silicate | Pargasite | 41.8 | 40.1 | 0.3 | 15.6 | 6.3 | <d.l. | 17 |
| | | Forsterite | 25.3 | 41.0 | <d.l. | <d.l. | 4.5 | <d.l. | 53 |
| | | Diopside | 13.1 | 51.0 | 0.4 | 2.7 | 2.2 | <d.l. | 16 |
| | | Serpentine | 8.6 | 41.9 | <d.l. | 0.2 | 2.4 | <d.l. | 39 |
| | | Phlogopite | 7.6 | 38.8 | 0.2 | 16.6 | 3.7 | <d.l. | 24 |
| | | Anhydrite | 3.0 | <d.l. | <d.l. | <d.l. | <d.l. | <d.l. | <d |
| | | Bornite | 0.3 | | | | | | |
| | | Hematite | 0.3 | | | | | | nA |
| | | Al-spinel | 0.04 | | | | | | nA |
| | | Magnetite | n.i. | <d.l. | 0.3 | <d.l. | 92.8 | 0.6 | 1. |
| | | Chlorite | n.i. | 34.2 | <d.l. | 13.4 | 2.9 | <d.l. | 35 |
| | | Spadaite | n.i. | 43.7 | <d.l. | <d.l. | 6.1 | <d.l. | 32 |
| | | **Recalulated volatile free bulk rock** | | **43.2** | | **8.7** | **4.9** | | **29** |
| FM1 | Mg-silicate skarn | Anhydrite | 75.7 | <d.l. | <d.l. | <d.l. | <d.l. | <d.l. | <d |
| | | Serpentine | 14.9 | 41.9 | <d.l. | 0.2 | 2.4 | <d.l. | 39 |
| | | Magnetite | 4.2 | <d.l. | 0.3 | <d.l. | 92.8 | 0.6 | 1. |
| | | Forsterite | 4.2 | 41.0 | <d.l. | <d.l. | 4.5 | <d.l. | 53 |
| | | Phlogopite | 0.7 | 38.8 | 0.2 | 16.6 | 3.7 | <d.l. | 24 |
| | | Sulfides | n.i. | | | | | | nA |
| | | **Recalulated volatile free bulk rock** | | **15.32** | | **0.09** | **8.45** | | **15.** |

812 apfu: atoms fer formula unit
813 <d.l. below detection limit
814 n.A. not analysed with FE-EPMA
815 n.i. not identified in QEMSCAN map
816 Mg#=100*Mg[mol]/(Mg[mol]+Fe[mol])
817 [1] Henley et al. (2017)

818

819

820

821 **Table 2.** Results of thermodynamic models for phase abundances and composition of calcite +

822 forsterite + diopside + phlogopite + spinel for CS1-Mg-rich-silicate and forsterite + diopside +

823 calcite + phlogopite + spinel + pargasite for sample FM1. Within the stability fields, a change in

824 fluid composition (and temperature) has minor effects on mineral modes and compositions. The

825 abundance and composition of mineral phases are here reported at peak metamorphic conditions

826 (750 °C and 51 MPa) and 50 mol% $CO_2$ in the interacting $H_2O$-$CO_2$ fluid.

| Sample | Mineral phases | Abundances of mineral phases per themodynamic modelling | | Composition per thermodynamic m | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Vol% | wt% | Number Oxygen | Si apfu | Al apfu | Fe apfu | Mg apfu | Ca apfu |
| Reconstructed bulk composition of FM1 | Calcite | 77.87 | 73.13 | 1 | | | | 0.001 | 0.999 |
| | Forsterite | 21.84 | 26.54 | 4 | 1.000 | | 0.466 | 1.534 | |
| | Diopside | 0.13 | 0.16 | 6 | 1.827 | 0.345 | 0.084 | 0.743 | 1.000 |
| | Phlogopite | 0.13 | 0.12 | 11 | 2.968 | 1.064 | 0.095 | 2.873 | |
| | Spinel | 0.04 | 0.05 | 4 | | 2.000 | 0.352 | 0.648 | |
| Reconstructed bulk composition of CS1-Mg-silicate | Forsterite | 33.23 | 35.22 | 4 | 1.000 | | 0.229 | 1.771 | |
| | Diopside | 17.43 | 18.08 | 6 | 1.968 | 0.071 | 0.032 | 0.929 | 0.994 |
| | Calcite | 3.52 | 3.01 | 1 | | | | 0.001 | 0.999 |
| | Phlogopite | 11.95 | 10.46 | 11 | 2.968 | 1.064 | 0.095 | 2.873 | |
| | Spinel | 1.31 | 1.54 | 4 | | 2.000 | 0.209 | 0.791 | |
| | Pargasite | 32.57 | 31.69 | 23 | 6.002 | 3.009 | 0.128 | 3.863 | 1.998 |

827