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### Petrochronology of Hydrothermal Rutile in Mineralized Porphyry Cu Systems

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#### Abstract

Hydrothermally formed rutile is a common mineral in porphyry Cu (-Au-Mo) deposits and has the potential to provide versatile information about the physical-chemical conditions and timing of mineralization. In this study, we investigated the trace element composition and U-Pb dates of hydrothermal rutile by LA-ICP-MS together with its petrographic context, in four well-studied porphyry systems: Batu Hijau (Indonesia), Bingham Canyon (USA), El Salvador (Chile) and Northparkes (Australia). A similar sequence of rutile generations occupying comparable textural positions was found to be common to all investigated deposits. We particularly focused on the most common rutile generation that is formed by the breakdown of biotite and temporally closely associated with mineralization as demonstrated by intergrowth relationships between individual, blocky rutile grains and Cu-Fe sulfides as well as cathodoluminescence imaging of mineralized quartz veins. Compositionally, rutile shows large trace element variations within and among the porphyry deposits, indicating that the compositions of both the local host rock and the fluid phase influence that of hydrothermal rutile. In comparison with non-hydrothermal rutile of various petrogenetic origins, rutile from porphyry Cu deposits show characteristic differences regarding their Sn, W, Si and Fe concentrations, indicating that rutile might be used to fingerprint porphyry-style mineralization. Due to its temporal link to Cu mineralization, texturally controlled in-situ U-Pb dating of blocky rutile grains by LA-ICP-MS provides the possibility to directly determine the absolute timing of Cu mineralization. Despite variable incorporation of initial Pb in the investigated hydrothermal rutile, we obtained robust lower intercept U-Pb dates that overlap within uncertainty with previously obtained mineralization ages for all four deposits, including those based on high-precision (ID-TIMS) zircon dating of bracketing porphyry intrusions. This demonstrates that rutile can be used to accurately predict the age of porphyry Cu deposit formation and with a precision better than 1.5% relative for deposits older than ca. 10 million years.

**Keywords:** Rutile; Porphyry Cu deposits; U-Pb dating; Cathodoluminescence; LA-ICP-MS; Mineral chemistry

#### 1. Introduction

Porphyry Cu deposits are the products of short-lived magmatic-hydrothermal systems operating in the upper crust and represent the major source for Cu and other critical metals such Au, Mo, Ag, and Re (Sillitoe, 2010). Their thermal evolution with time is of fundamental interest for ore formation due

to the temperature dependence of metal solubility in aqueous solutions (e.g., Crerar and Barnes, 1976; Hemley et al., 1992; Liu and McPhail, 2005). Besides a characteristic sequence of mutually cross-cutting vein types (Gustafson and Hunt, 1975) and abundant fluid inclusions in hydrothermal quartz (e.g., Roedder, 1971; Nash, 1976), concentrically arranged alteration zones surrounding the causative porphyritic stocks document the thermal evolution of the hydrothermal system on the deposit scale (Lowell and Guilbert, 1970; Seedorff et al., 2005; Sillitoe, 2010). On the scale of a hand-specimen, multiple sequentially overprinting alteration styles are commonly present and associated with different vein types, enabling the establishment of a relative time sequence. Changes in alteration mineralogy with time give insights into the evolution of the magmatic fluid in time and space (e.g., Gustafson and Hunt, 1975; Zaluski et al., 1994; Idrus et al., 2009; Reed et al., 2013; Maydagán et al., 2016). Alteration minerals that formed contemporaneously with Cu mineralization can provide comprehensive information about prevailing conditions during ore formation.

In many porphyry Cu deposits, hydrothermal rutile occurs in different alteration zones due to the breakdown of primary TiO<sub>2</sub>-bearing mineral phases (e.g., Czamanske et al., 1981; Force et al., 1984; Scott, 2005; Rabbia et al., 2009). Czamaske et al. (1981) documented that rutile abundance and grain size follows Cu ore grade distribution in several porphyry systems, indicating a genetic link between mineralization and rutile formation. Recent detailed petrographic work showed that hydrothermal rutile mainly formed by the breakdown of biotite contemporaneously with moderate-temperature (approximately 400° to 300°C) sulfide precipitation at the Batu Hijau porphyry Cu deposit (Schirra et al., in revision). Hydrothermal rutile is commonly U-rich and, as such, can be used for dating (e.g., Schandl et al., 1990; Vry and Baker, 2006; Zack et al., 2011), while its trace element content can help elucidate hydrothermal processes (e.g., Rabbia et al., 2009) associated with porphyry-style mineralization (e.g., Czamanske et al., 1981; Force et al., 1984; Scott, 2005; Kelley et al., 2011).

Despite its abundance in porphyry systems (e.g., Force, 1980; Czamaske et al., 1981) and peculiar geochemical composition reported from various types of hydrothermal ore deposits (e.g., Clark and Williams-Jones, 2004; Plavsa et al. 2018; Agangi et al., 2019), there was little attempt in using the trace element signature of rutile as a systematic petrogenetic indicator in porphyry-type deposits. Moreover, while rutile has long been used as a direct U-Pb chronometer to date mineralization in other deposit types such as volcanogenic massive sulfide (e.g., Schandl et al., 1990), stratiform Cu mineralization (e.g., Richards et al., 1988) or various types of gold deposits (e.g., de Ronde et al., 1991; Wong et al., 1991; Norcross et al., 2000, Pi et al., 2017), it has never been systematically tested for porphyry Cu systems.

In this study, we apply in-situ LA-ICP-MS microanalysis to petrographically well-characterized, individual rutile grains from highly mineralized rock samples from several world-class porphyry Cu deposits, namely Batu Hijau (Indonesia), Bingham Canyon (USA), El Salvador (Chile), and Northparkes

(Australia). The goals of this study are to 1) gain insight into hydrothermal processes recorded by rutile trace element variations, 2) assess the potential of rutile to directly date the hydrothermal activity and Cu mineralization, and 3) test the applicability of rutile geochemistry as potential exploration tool for porphyry-style mineralization. Detailed petrography, including cathodoluminescence (CL) imaging, indicates that hydrothermal rutile occupies similar textural positions in all four investigated porphyry systems and that the main rutile-forming event coincides with moderate-temperature mineralization. Consequently, U-Pb rutile dating by LA-ICP-MS enables texturally controlled, direct dating of moderate-temperature Cu-Fe sulfide precipitation in porphyry Cu systems.

#### 2. Geological and Chronological Background of Investigated Porphyry Systems

Samples from the hydrothermally altered, mineralized zones of the Batu Hijau, Bingham Canyon, El Salvador and Northparkes deposits were screened for rutile in this study. The geological framework and previous geochronological studies of the individual deposits are briefly outlined below.

#### 2.1. Batu Hijau

The Batu Hijau porphyry Cu-Au deposit is located in SW Sumbawa, Indonesia (Meldrum et al., 1994). Mineralization and alteration are centered on a tonalite complex that intruded into volcanoclastic sequences along the contact with a precursor intrusion of equigranular quartz-diorite (Mitchell et al., 1998; Clode et al., 1999). The tonalite complex is divided into three consecutive intrusions called Old (OT), Intermediate (IT) and Young Tonalite (YT). Mineralization is mainly associated with the OT and IT, whereas the YT crosscuts high Cu and Au grades and displays weak hydrothermal overprint and mineralization (Clode et al., 1999).

Garwin (2000) used SHRIMP U-Pb dating of zircon and  ${}^{40}$ Ar/ ${}^{39}$ Ar dating of hydrothermal biotite and sericite to respectively constrain the ages of the tonalite intrusions (3.76 ± 0.10 Ma for OT to 3.67 ± 0.12 Ma for YT) and hydrothermal alteration (3.73 ± 0.08 Ma for biotite to 3.65 ± 0.02 Ma for sericite). Recent high-precision CA-ID-TIMS U-Pb zircon dating bracketed the duration of the mineralization process to a maximum of 122 ka between the OT (3.736 ± 0.023 Ma) and YT (3.646 ± 0.022 Ma; Large et al., 2020).

Economic sulfides are mainly hosted by high-temperature quartz veins associated with biotite – magnetite alteration (Clode et al., 1999; Arif and Baker, 2004) but CL imaging revealed that the majority of these sulfide grains are genetically linked to hairline-thin veinlets, which appear as rather inconspicuous cracks partially filled by Cu-Fe sulfides, associated with chlorite – sericite alteration selvages and crosscut or re-open earlier quartz veins (Schirra et al., in revision). Rutile is commonly present within or along these veinlets, probably as a product of biotite alteration to chlorite and sericite. Therefore, rutile is assumed to have formed at the same time as a significant part of the Cu-Fe sulfides.

#### 2.2. Bingham Canyon

Hydrothermal activity at the Bingham Canyon porphyry Cu-Au-Mo deposit, Utah, is related to the multiphase Bingham Stock, which intruded into a sedimentary sequence (Butler, 1920; Babcock et al., 1995; Redmond and Einaudi, 2010). The Bingham Stock consists of an early equigranular monzonite (EGM) intrusion, which is crosscut by five successive porphyry intrusions: Quartz monzonite porphyry (QMP), latite porphyry (LP), quartz latite porphyry (QLP), biotite porphyry, and quartz latite porphyry breccia (Moore and Czamanske, 1973; Babcock et al., 1995; Redmond and Einaudi, 2010). The QMP displays the most intense hydrothermal overprint and highest ore grades, which extend into the premineralization EGM and sedimentary units. The other porphyry intrusions are volumetrically minor and show decreasing vein densities, alteration intensity and ore grade towards the youngest, only weakly mineralized and partially unaltered latite porphyry breccia (Redmond and Einaudi, 2010).

Zircon TIMS U-Pb dating yields an age of the EGM of  $38.55 \pm 0.19$  Ma, supported by a  $38.40 \pm 0.19$  Ma  $^{40}$ Ar/ $^{39}$ Ar plateau age for primary biotite (Parry et al., 2001). The individual porphyry dykes have been dated by CA-ID-TIMS of zircon indicating a short time interval of 320 ka for porphyry emplacement and Cu-Au ore formation between 38.10 to 37.78 Ma (von Quadt et al., 2013). Recent high-precision CA-ID-TIMS U-Pb zircon dating of the QMP, LP and QLP intrusions refined the maximum duration of Cu-Au mineralization to 662 ka (Large, 2018). A Re-Os age of molybdenite within the QMP revealed an age of  $37.00 \pm 0.27$  Ma (Chesley and Ruiz, 1998).

Several authors have reported the presence of rutile throughout the Bingham Canyon deposit (Stringham, 1953; Moore and Czamanske, 1973; Lanier et al., 1978; Maughan et al., 2002). In general, two types of rutile have been distinguished: sagenetic rutile, which forms oriented, thin, elongated crystals within igneous biotite in altered and unaltered rocks (e.g., Maughan et al., 2002) and blocky/stubby rutile associated with partially altered igneous and hydrothermal biotite (e.g., Stringham, 1953). An overall increase in rutile abundance and size of individual crystals with depth and ore grades has been reported by Czamanske et al. (1981).

#### 2.3. El Salvador

The porphyry Cu-Mo deposit at El Salvador, Chile, is centered on an Eocene composite porphyritic granodiorite complex that intruded into Cretaceous and lower Tertiary volcanic-sedimentary rocks of the Indio Muerto district. Four porphyritic intrusions of decreasing age, the X, K, L and A porphyries, are related to alteration, veining and mineralization, whereas latite or dacite porphyritic dykes post-date ore formation (Gustafson and Hunt, 1975; Cornejo et al., 1997). The X porphyry intrusion is interpreted to pre-date the main mineralization event, which was temporally related mainly to the emplacement of the K porphyry and in a lesser extent to the younger L and A porphyries that are associated with lower Cu grades and less intense alteration (Gustafson and Hunt, 1975).

Dating of all intrusions by variable methods indicates an age of about 42 Ma for the El Salvador deposit (Gustafson and Hunt, 1975; McWilliams, 1994, 1996; Cornejo et al., 1997; Gustafson et al., 2001). More recent, SHRIMP-RG U-Pb zircon dating yielded ages of  $43.6 \pm 0.4$  Ma for the X porphyry followed by the K porphyry at  $42.9 \pm 0.4$  Ma and  $42.3 \pm 0.5$  Ma and the L porphyry at  $42.4 \pm 0.6$  Ma and  $42.2 \pm 0.5$  Ma (Lee et al., 2017). Re-Os ages of hydrothermal molybdenite suggest that molybdenite mineralization occurred between 41.8 and 41.2 Ma (Zimmermann et al., 2014).

The hypogene ore body at El Salvador is zoned similarly to the one at Batu Hijau with a bornite + chalcopyrite-rich core hosted by potassic altered rock grading outwards to chalcopyrite-dominated sulfide assemblages overlapping with the chlorite – sericite alteration zone (Gustafson and Hunt, 1975). Rutile has been reported to be present within the alteration halos of all vein types in El Salvador (Gustafson and Hunt, 1975; Gustafson and Quiroga, 1995). The breakdown of ilmenite to rutile plus hematite and the replacement of sphene by rutile plus anhydrite or calcite are assumed by these authors to be the major rutile-producing processes.

#### 2.4. Northparkes

At Northparkes in the Goonumbla district of New South Wales, Australia, composite quartz monzonite porphyries (QMP) host multiple economic Cu-Au anomalies within a small area of around 10 km<sup>2</sup>. All porphyries are rooted in a pre-mineralization, granite to quartz-monzonite pluton, emplaced into Ordovician volcanic rocks (Heithersay and Walshe, 1995; Lickfold et al., 2003). The QMP complexes include in relative time sequence early biotite QMP, K-feldspar QMP, and augite-biotite-K-feldspar QMP (Lickfold et al., 2003). The K-feldspar and augite – biotite – K-feldspar QMP host the highest ore grades associated with the highest vein densities and most intense alteration overprint (Heithersay and Walshe, 1995; Lickfold et al., 2003, 2007). Volumetrically minor monzonite porphyry dikes, termed zero porphyries, represent the youngest phase of intrusive activity at Northparkes, post-dating the Cu-Au mineralization.

The Northparkes deposits are of Late Ordovician to Early Silurian age and one of the oldest wellpreserved porphyry copper deposits. Radiometric dating studies have produced an age range from 455 to 435 Ma for emplacement of the various intrusions and associated alteration using mainly  $^{40}$ Ar/ $^{39}$ Ar dating of hornblende, biotite and sericite as well as U-Pb SHRIMP dating of zircons (Perkins et al., 1990; Butera et al., 2001; Lickfold et al., 2003, 2007). Lickfold et al. (2007) bracketed the mineralization period by U-Pb SHRIMP zircon dating of the biotite quartz monzonite (444.2 ± 4.7 Ma) and a Zero porphyry dyke (436.7 ± 3.3 Ma). Most recently, Pacey et al. (2019) used Rb-Sr dating of epidotes and whole rock samples from the propylitic alteration zones, providing a rough estimate of 450 ± 11 Ma for hydrothermal activity at Northparkes.

All deposits at Northparkes share common hydrothermal features, including veining sequence, alteration patterns and mineralization style (Heithersay and Walshe, 1995). The ore bodies consist of

a bornite-rich center, surrounded by a chalcopyrite-rich zone that transitions outward to the pyritedominated periphery. Based on textural observations, ore-grade mineralization is interpreted to be related to quartz – K-feldspar – sulfide veins associated with pervasive potassic alteration (Pacey et al., 2019). Rutile is abundant and interpreted to be the result of biotite and titanoferous magnetite alteration. Size and geochemical composition of rutile, in particular high V contents, have been shown to be indicative for porphyry-style mineralization at Northparkes (Scott, 2005).

#### 3. Samples and Analytical Methods

The porphyry deposits included in this study were selected based on their spread in reported formation ages (Neogene to Early Silurian/Late Ordovician), their different geotectonic settings (intraoceanic vs. continental arc) and metal endowments (Cu-Au vs. Cu-Mo vs. Cu-Au-Mo). In addition, the timing and duration of hydrothermal activity at Batu Hijau and Bingham Canyon have been precisely bracketed by recent zircon CA-ID-TIMS dating (Large, 2018; Large et al., 2020), allowing robust assessment of the U-Pb rutile dating accuracy.

Most samples used in this study are inherited from earlier sample collections used for fluid inclusion studies at ETH Zürich. One or several samples were selected for each deposit, preferably from the highgrade ore shell. Polished thin and thick sections were prepared for further petrographic and analytical work. A brief sample description is given in Table 1.

Conventional transmitted and reflected light petrography was carried out at ETH Zürich to find rutile grains and to identify their textural relationship with other alteration minerals and economic sulfides. Subsequently, Secondary Electron (SE), Back-Scattered Electron (BSE) and CL imaging were conducted using a JEOL JSM 6390 LA secondary electron microscope equipped with a Deben Centaurus CL detector at an acceleration voltage of 15 kV. Some of the identified grains were checked for TiO<sub>2</sub> polymorphs by acquiring Raman spectra using a 532 nm DPSS laser and a Dilor LabRam Instrument attached to an Olympus BX40 microscope. Obtained spectra were compared with reference spectra of rutile, anatase and brookite from the RRUFF database (Lafuente et al., 2015). Only a small fraction (< 5%) of the identified grains were assigned as anatase and these showed no significant differences in trace element composition compared to rutile. Furthermore, anatase could also be microscopically identified with great confidence due to its very pale, slightly greenish color compared to the heavily colored rutile grains. Therefore, we did not check systematically every grain with the Raman. Brookite in contrast was never present in the investigated porphyry samples.

Analyses of rutile U–Pb isotopic compositions and trace element concentrations were carried out at ETH Zürich, Switzerland by laser ablation – inductively coupled plasma – sector field – mass spectrometry (LA-ICP-SF-MS) using a RESOlution S-155 (ASI/Applied Spectra) 193 nm ArF excimer laser system attached to an Element XR (Thermo) sector-field ICP-MS. We used a laser repetition rate of 4 Hz, a spot diameter of 51 µm (for U-Pb dating) or 19 µm (for trace elements) and a laser energy density on sample of ca. 4 J/cm<sup>2</sup>. The sample surface was cleaned immediately before each analysis by three pre-ablation pulses. Ablation was performed in a dual-volume, fast-washout S-155 ablation cell (Laurin Technic) fluxed with carrier gas consisting of ca. 0.5 L/min He and make-up gas consisting of ca. 1 L/min Ar and 2 mL/min N<sub>2</sub>. The ablated aerosol was homogenized via flushing through an in-house squid device before being introduced in the plasma. The ICP-MS instrument was optimized for maximum sensitivity on Pb, Th and U while keeping low the production of oxides (<sup>248</sup>ThO<sup>+</sup>/<sup>232</sup>Th<sup>+</sup> ≤0.25%) and the U/Th ratio at ca. 1 (on NIST SRM612 glass). A typical measurement consisted in 25 s of background measurement followed by 40 s of sample ablation for U-Pb dating and 30 s for trace elements. For trace elements, we have recorded intensities for the following isotopes: <sup>23</sup>Na, <sup>27</sup>Al, <sup>29</sup>Si, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>107</sup>Ag, <sup>118</sup>Sn, <sup>121</sup>Sb, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, <sup>156</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>173</sup>Yb, <sup>175</sup>Lu, <sup>180</sup>Hf, <sup>181</sup>Ta, <sup>182</sup>W, <sup>208</sup>Pb, <sup>232</sup>Th and <sup>238</sup>U. For U-Pb dating, intensities for <sup>238</sup>U, <sup>235</sup>U, <sup>207</sup>Pb and <sup>206</sup>Pb were measured.

For U-Pb dating, the resulting intensities were processed offline with the Igor Pro Iolite v2.5 software (Hellstrom et al., 2008), using the VizualAge data reduction scheme (Petrus and Kamber, 2012). Background-subtracted intensities were used to calculate isotope ratios, which were corrected for laser-induced Pb/U fractionation (after Paton et al., 2010), instrumental mass discrimination and drift by conventional standard-sample bracketing, against rutile reference material R10 (using isotope ratios from Luvizotto et al., 2009). No common Pb correction was carried out and dates were interpreted by the lower intercept method in Tera-Wasserburg diagrams. Data from secondary rutile reference materials R13 (Schmitt and Zack, 2012) and WOD-B (in-house) were processed as unknowns to check the accuracy of the corrections. Age calculations and data plotting were performed using the IsoplotR toolkit (Vermeesch, 2018). The data from unknowns and rutile reference materials are provided in the Supplementary Table. Systematic uncertainties were propagated on the final dates (as discussed in Zack et al., 2011) using the same protocol as conventionally applied for zircon U-Pb geochronology (Horstwood et al., 2016), i.e. by quadratic addition of relative uncertainties on (i) the final lower intercept date obtained using IsoplotR; (ii) the <sup>235</sup>U and <sup>238</sup>U decay constants, known to a high precision (< 0.1% relative; Jaffey et al., 1971); (iii) the isotopic ratios of the calibration reference material (set to 0.5% based on ID-TIMS data of Luvizotto et al., 2009) and (iv) the long-term excess variance of secondary rutile reference materials (0.8% based on 8 analytical sessions over a period of 2 years).

For trace elements, the intensities were processed offline using the Matlab-based SILLS software (Guillong et al., 2008). The NIST SRM610 glass (Jochum et al., 2011) was used to quantify element concentrations and correct for instrumental drift via conventional standard-sample bracketing. A  $TiO_2$  concentration of 99 wt.% was used as internal standard for relative sensitivity correction. A further matrix effect correction factor (of typically < 10% relative) was applied by comparing the average

concentrations obtained on rutile reference material R10 (measured as an unknown) and the recommended values of Luvizotto et al. (2009). The USGS GSD-1G glass (Guillong et al., 2005) was used as a validation reference material to check accuracy and reproducibility. Data is provided in the Supplementary Table.

#### 4. Results

#### 4.1. Microtextural Context of Rutile

In all investigated porphyry deposits rutile occurs in similar textural positions and mineral parageneses. Morphologically, two types of rutile can be distinguished: 1) needle-like rutile with very high aspects ratios  $\geq$ 10 (e.g., Fig. 1D), and 2) blocky rutile with aspect ratios  $\leq$  10 (Fig. 1). Needle-like rutile occurs exclusively within igneous biotite and hydrothermal quartz. In biotite, rutile needles follow cleavage planes, resulting in a triangular mesh network structure (sagenetic rutile, Fig. 1D), whereas rutile needles in quartz are typically randomly oriented and can be slightly bent. Needle-shaped rutile was generally too small to be targeted for LA-ICP-MS analyses and is hence not further considered in this study.

Blocky rutile occurs in three different textural positions:

- (1) Most commonly, elongated, prismatic or equidimensional, rounded rutile grains are hosted by chlorite and/or sericite partially or completely replacing igneous and hydrothermal biotite (Fig. 1 and 2). These rutile grains can be aligned along former cleavage planes or be randomly distributed and their sizes can vary from < 10 to > 500  $\mu$ m. Unaltered biotite rarely hosts blocky rutile grains. Most rutile grains that appear to be hosted by biotite are typically associated with biotite-replacing alteration minerals on the micro-scale (e.g., Fig. 2).
- (2) Rutile may form in clusters up to a few millimeters in size that are associated with Cabearing minerals, such as anhydrite, calcite and apatite (Fig. 1L). Most individual rutile grains are typically between 20 to  $200 \ \mu m$  in size.
- (3) Some individual rutile grains are hosted within hydrothermal quartz veins. These are rare compared to the other two textural positions. CL imaging reveals the spatial association of these rutile grains with a specific quartz generation characterized by comparatively dull luminescence. The dull-luminescent quartz generation crosscuts and truncates growth zones of bright luminescent quartz, besides rutile also hosts Cu-Fe sulfides and is present in all investigated porphyry Cu deposits (Fig. 3). Rutile within quartz veins ranges in size from < 10 to 100 μm.</p>

In all textural positions, blocky rutile can be intergrown with or included in sulfides (Fig. 1A to C and I to L). Blocky rutile from all deposits contains mineral and fluid inclusions. Mineral inclusions are most

commonly ilmenite and monazite-Ce, rarely apatite and anhydrite (e.g., Fig. 1F). Sulfide inclusions have not been observed. Rounded or irregular fluid inclusions (< 10  $\mu$ m) are exclusively two-phase, highdensity (small bubble, < 30 vol.%), low- to moderate-salinity (no halite cubes, < 26 wt.% NaCl<sub>eq</sub>.) fluid inclusions (Fig. 4). Optically, they resemble aqueous inclusions hosted by dull-luminescent quartz described from Batu Hijau (Schirra et al., in revision).

Optical microscope and SEM observations reveal that rutile grains are mostly unzoned. Only a few grains show irregular, patchy zoning with areas relatively enriched in Si and Fe (based on EDS spectra, Fig. 1F). Oscillatory or sector zoning are rare and, wherever present, also chemically defined by zones enriched in Si and Fe.

#### 4.2. LA-ICP-MS U-Pb Dating

More than 500 U-Pb measurements were conducted on hydrothermal rutile grains of clear textural context from all deposits. Results are reported in Table 2 and illustrated in figure 5. The U-Pb data, calculated ages and uncertainties of single-grain analyses can be found in the Supplementary Table. Only the largest rutile grains (>50  $\mu$ m) were targeted for U-Pb dating due to the use of a larger spot diameter than for trace elements.

Rutile U-Pb isotopic compositions from all deposits suffer from a strongly variable but generally high proportion of common lead (Pb<sub>c</sub>) as reflected by the spread of the discordant data points in the Tera-Wasserburg ( $^{207}$ Pb/ $^{206}$ Pb vs.  $^{238}$ U/ $^{206}$ Pb) diagram (Fig. 5). This spread is generally interpreted as reflecting a mixture, in different proportions, of common and radiogenic Pb, in which case the lower intercept of the data regression line with the Concordia marks the inferred crystallization age of the population (e.g., Schoene, 2014). In theory, a Pb<sub>c</sub> correction based on the <sup>208</sup>Pb intensity is possible in the case of rutile that contains very little, if any Th, so that thorogenic lead can be considered as negligible (Zack et al., 2011). However, this correction still requires assuming a certain Pb<sub>c</sub> isotopic composition (Zack et al., 2011), which is not straightforward for such a fluid-mobile element in multicomponent, magmatic-hydrothermal porphyry Cu systems. In addition, uncertainties on the composition and fraction of Pb<sub>c</sub> should be propagated to the final common Pb-corrected date (Andersen, 2002). Given the very large data spread in U/Pb<sub>c</sub> ratios for all samples, the common Pb correction based on <sup>208</sup>Pb would arguably yield less precise results than the lower intercept method, so that the latter was preferred.

For all four deposits, the rutile data linear regression arrays with MSWD's comprised between 1.0 and 1.7 (Fig. 5). For Batu Hijau, Bingham Canyon and El Salvador, rutile U-Pb data were obtained from three distinct samples, but individual dates were systematically overlapping within uncertainty for each deposit (see Fig. 5). Therefore, we pooled the data from all samples together for these deposits to calculate single lower intercept dates. These are respectively of  $3.60 \pm 0.15$  Ma ( $2\sigma$ ; n = 187; MSWD

= 1.2) for Batu Hijau; 38.09  $\pm$  0.49 Ma (2 $\sigma$ ; n = 114; MSWD = 1.7) for Bingham Canyon; 42.11  $\pm$  0.50 Ma (2 $\sigma$ ; n = 144; MSWD = 1.6) for El Salvador, and 442.2  $\pm$  4.8 Ma (2 $\sigma$ ; n = 46; MSWD = 1.0) for Northparkes.

#### 4.3. Trace Element Systematics

Some trace elements analyzed in rutile grains show suspiciously high concentrations and intercorrelations (e.g., Al and Si; Fig. 6A) indicative for potential contamination of the signal, either by accidental ablation of neighboring mineral phases or due to the presence of micro-inclusions observed by SEM. The resulting element intensity changes are generally easy to detect and exclude from the time-integrated signals (Fig. 7) during data reduction. This is not always the case, especially if the volume of ablated rutile relative to another phase remains roughly constant throughout the ablation, producing an apparently homogeneous, yet contaminated signal. Likewise, numerous tiny (< 1  $\mu$ m) inclusions would elevate the overall abundance of certain elements without showing clearly distinguishable peaks. Many rutile analyses show unusually high, apparent Al and Si concentrations (> ~1000  $\mu$ g/g) that are positively correlated to each other, and to some extent to Na contents (Fig. 6B), suggesting that Al- and/or Na-rich silicates (chlorite, sericite, plagioclase) might be common contaminants. Extremely high Si values that do not correlate with Al are most likely caused by partial ablation of quartz. The moderate correlation between Na, Zn and Cu (Fig. 6) points towards a potential ablation of small fluid inclusions. A few unreasonably high Fe contents might be due to partial ablation of ilmenite intergrown with rutile.

These sources of contamination did not affect most of the important rutile-hosted trace elements like Zr, Hf, Mo, W, Sn, Nb, Ta, V, Cr, Y, and REE, so that contaminated rutile grains are not highlighted in other trace element diagrams presented here and not considered for further discussion.

As a first step, principal component analysis (PCA), a statistical method to reduce the dimensionality of multivariate compositional datasets (e.g., Grunsky, 2010), was applied to our hydrothermal rutile trace element database in order to identify similarities and differences between the porphyry Cu deposits as well as trace element intercorrelations (Fig. 8). The PCA results show that trace element concentrations in rutile from the investigated porphyry systems show significant variations, both within and among individual deposits. When rutile grains from the four investigated deposits are considered together, the first two principal components capture approximately 64 % of the data variability (Fig. 8A). PC1 is predominantly defined by the well-correlated HFSE (Ta, Nb, Zr, Hf) as well as refractory metals (Cr, Mo, W), U and to a lesser extent V, whereas PC2 is defined by a combination of mainly Sn and Sb (Fig. 8B). The contributions of each element to the first four principal components are listed in table 3. Differences between individual deposits lie mostly in the PC1 value, which on average decreases from Bingham Canyon to El Salvador and Northparkes, with Batu Hijau clearly showing the lowermost values. In contrast to the other deposits, rutile from Batu Hijau appears to

show a greater spread along the PC2 axis in figure 8A, indicating that Sn and Sb, potentially in combination with W and Cr, explain most of the variation.

Figures 8C to F show PCA results for individual deposits, which show significant differences between one another in agreement with the observations above. Indeed, PCA for the rutile data from Batu Hijau (Fig. 8C) indicates that PC1 is defined by positively correlated Sn, V, Sb, Cr, W, and U concentrations, whereas PC2 is defined by well positively correlated concentrations of Zr and Hf with a lesser contribution of Mo. Niobium and Ta are positively correlated to each other but less well with Zr and Hf. For all other deposits (Fig. 8D to F), PC1 is mainly defined by positively correlated HFSE and to lesser extend by U and Mo. At Bingham Canyon, W contributes to PC1 but shows a slight negative correlation with Ta, Nb, Zr, Hf and U (Fig. 8D). PC2 is mainly defined by positively correlated concentrations of V and Sb. At El Salvador in contrast V and Sb are negatively correlated and contribute to a lesser extent to PC2, which is mainly defined by negatively correlated concentrations of Cr and Fe (Fig. 8E). Rutile from Northparkes appears to show positive correlations between Sn, Mo, U, Ta, Nb, Zr and Hf, which collectively define PC1, whereas PC2 is mainly defined by positively correlated Fe and W, which are negatively correlated with V.

Some of these general trace element characteristics are also highlighted in figures 9 and 10. In general, rutile from all four porphyry systems are characterized by Nb, Fe, Si, W, V, and Cr concentrations >1000 and up to 10,000  $\mu$ g/g, and Zr, Al, Ta, and Sn concentrations between 10 and 1000  $\mu$ g/g. Antimony, Hf and U are typically in the range of 1 to 100  $\mu$ g/g, and Na and Zn were commonly detected. Metals such as Mn, Cu, and Pb also vary between 1 to 100  $\mu$ g/g but were detected in less than 50% of the analyses. In the sub- $\mu$ g/g range, Y and Th were commonly detected, Ag only sporadically. Rare earth elements (REE) were frequently detected with concentrations typically between 0.01 and 10  $\mu$ g/g. Only La, Ce, and Nd can occasionally reach concentrations up to 100  $\mu$ g/g, which do not appear to be caused by mineral inclusions in the time-integrated LA-ICP-MS signals. The chondrite-normalized REE+Y spider diagrams show slightly fractionated patterns for rutile from most investigated porphyry Cu deposits (La<sub>N</sub>/Yb<sub>N</sub> = 2 to 6), except Bingham Canyon rutile that shows moderate fractionation (La<sub>N</sub>/Yb<sub>N</sub> ~20; Fig. 10A). A pronounced negative Y anomaly is visible in all deposits and a slightly positive Eu anomaly in rutile from Batu Hijau and El Salvador (Fig. 10A).

#### 5. Discussion

#### 5.1. Origin of Rutile and Its Relation to Mineralization

Besides the first generation of needle-like rutile in biotite and quartz that formed by exsolution of excess Ti during cooling (e.g., Shau et al., 1991), the other two generations of blocky crystals targeted for analyses most certainly reflect hydrothermal rutile formed by the breakdown of Ti-rich minerals (Williams and Cesbron, 1977; Czamanske et al., 1981; Force, 1991). Regarding the clustered rutile

grains, the mineral association and textures (rutile cemented by Ca-rich minerals; Fig. 1F) indicate pseudomorphic replacement of igneous titanite as indicated by the di-pyramidal shape of these clusters. Titanite replacement by rutile and Ca-rich minerals occurs during potassic alteration in the presence of oxidizing S-rich high-temperature fluids (e.g., Force, 1991).

The third rutile generation is spatially associated with chlorite and/or white mica and presumably formed by alteration of Ti-rich biotite (Fig. 1 D to F and Fig. 2). High Ti concentrations in igneous and hydrothermal biotite from Batu Hijau (2 to 3.5 wt.% TiO<sub>2</sub>; Mitchell et al., 1998) and Bingham (1.5 to 6 wt.% TiO<sub>2</sub>; Moore and Czamanske, 1973) are typical for biotite from porphyry systems (e.g., Jacobs and Parry, 1979; Selby and Nesbitt, 2000). In addition, hornblende, which is replaced by secondary biotite during potassic alteration, might contribute to the formation of rutile (e.g., Force, 1984; Rabbia et al., 2009). However, relatively high Ti concentrations of several weight percent in secondary biotite (e.g., Czamanske et al., 1981; Idrus, 2018) indicate that most of the Ti originally hosted in mafic minerals like hornblende is passed on and incorporated in the forming biotite, although minor formation of rutile during potassic alteration cannot be ruled out. Ilmenite laths, rather than rutile, have been found in association with magnetite, indicating that re-equilibration of Ti-rich magnetite probably did not significantly contribute to rutile formation. The formation process of the different rutile generations is schematically illustrated in figure 14.

From the above discussion, rutile forms throughout the lifespan of the hydrothermal system, from the potassic alteration stage at temperatures > 500°C to the sericite alteration stage down to ca. 300°C (Fig. 14). Particularly, blocky rutile that formed predominantly by the breakdown of biotite is considered to form contemporaneously with major Cu-sulfide precipitation at similar temperatures (i.e., 400° to 300°C). Textural relationships clearly confirm the co-existence of rutile and Cu-Fe sulfides at Batu Hijau, Bingham Canyon, El Salvador and Northparkes (Fig. 1 and 3). At Batu Hijau at least a significant amount of the economic sulfides formed at moderate temperatures (360° to 310°C), coinciding with biotite-destructive chlorite – sericite alteration and formation of a distinctively dullluminescent quartz generation (Schirra et al., in revision). At Bingham Canyon, a spatial relationship has also been previously reported between dull-luminescent quartz and economic sulfide grains formed at a similar temperature range (Landtwing et al., 2005, 2010). Blocky rutile formed coevally with such mineralization, as it is systematically associated with both, biotite-destructive alteration mineralogy and dull-luminescent quartz hosting Cu-Fe sulfides in the investigated samples. Czamanske et al. (1981) reported that abundance and grain size of rutile correlate with ore grades in several porphyry Cu deposits, supporting the temporal relationship between rutile formation and sulfide precipitation.

The abundance and distribution of rutile in porphyry systems likely depend on the  $TiO_2$  concentration of the host rocks, the nature of the primary Ti-rich minerals, and the alteration type and

intensity (e.g., Rabbia et al., 2009). Although this cannot be studied in detail here due to the limited amount of samples, the fact that rutile is a product of typical porphyry-related hydrothermal reactions and occupies similar textural positions in all studied deposits supports our first-order conclusion that it formed systematically synchronous with Cu mineralization.

#### 5.2. Texturally Controlled U-Pb Rutile Dating of Porphyry-Style Mineralization

In every studied porphyry Cu deposit, rutile U-Pb isotopic data define a single regression array between common and radiogenic Pb compositions with a MSWD close to 1 (Fig. 5), indicating that within uncertainties, the analyzed rutile grains belong to a single, co-genetic population of crystals within each individual porphyry deposit and that they did not lose radiogenic lead. The lower intercept date corresponds to the crystallization age of the rutile population, which, insofar it formed coevally with sulfide precipitation and biotite-destructive alteration, yields robust ages for Cu mineralization. In the following, we compare our rutile-based mineralization ages with previous age determinations using different dating methods for all investigated porphyry deposits (Fig. 5).

Rutile from Batu Hijau contains the lowest amount of U (Fig. 8A, B and 9F), while fluid and mineral inclusions are abundant (e.g., Fig. 4), which in combination with the young age and related low radiogenic Pb content, result in an elevated age uncertainty of around 4% relative. However, the obtained age of  $3.61 \pm 0.20$  Ma is consistent with high-precision U-Pb zircon dating of zircons from the causative tonalite intrusions, i.e., between the mineralized OT ( $3.736 \pm 0.022$  Ma) and the weakly mineralized YT ( $3.646 \pm 0.023$  Ma; Large et al., 2020). Although overlapping within uncertainty, the rutile U-Pb age is slightly shifted to the young side, which might be due to an initial deficit of <sup>230</sup>Th and hence of <sup>206</sup>Pb (Schärer, 1984). Initial <sup>230</sup>Th/<sup>238</sup>U disequilibrium may be caused by the distinct solubilities of U and Th in aqueous fluids (e.g., Ludwig et al., 2011) and fractionation during hydrothermal rutile growth (Brenan et al., 1994). In the case of Th-poor minerals like rutile, the maximum extent of the age correction for <sup>230</sup>Th disequilibrium is 110 ka (Schoene, 2014), which would shift the Batu Hijau rutile age to  $3.72 \pm 0.20$  Ma. The effect of <sup>230</sup>Th/<sup>238</sup>U disequilibrium on the calculated age becomes negligible for older samples, so that it was not considered in the interpretation of the rutile ages for the other deposits.

At Bingham Canyon, high-precision zircon dating of the porphyry intrusions bracket the mineralization age between the intrusion of the highly mineralized QMP ( $38.284 \pm 0.024$  Ma) and the post-mineralization QLP ( $37.736 \pm 0.057$  Ma; Large, 2018). The obtained rutile age of  $38.09 \pm 0.49$  Ma falls within this maximum time span of mineralization but is significantly older than the  $^{40}$ Ar/ $^{39}$ Ar age of hydrothermal biotite from the QMP ( $37.07 \pm 0.21$  Ma; Parry et al., 2001) and the Re-Os age of molybdenite ( $37.0 \pm 0.27$  Ma; Chesley et al., 1997). Molybdenite mineralization at Bingham Canyon occurs in later quartz-molybdenite veins associated with biotite alteration that crosscut earlier Cu-Fe

sulfide-bearing veins as well as the QLP dikes (Seo et al., 2012). Consequently, the reported Re-Os and <sup>40</sup>Ar/<sup>39</sup>Ar ages might not be representative for the apparently older Cu-Au mineralization.

For the El Salvador and Northparkes deposits, high-precision CA-ID-TIMS U-Pb zircon ages are not available. Ages for the porphyry intrusions at El Salvador have been obtained using U-Pb zircon SHRIMP dating and span a range of approximately 3 Ma from the X porphyry at 43.6  $\pm$  0.4 Ma over the K and L porphyries at 42.55  $\pm$  0.75 Ma and 42.35  $\pm$  0.65 Ma, respectively, to a post-mineralization latite dike at 41.6  $\pm$  0.5 Ma (Lee et al., 2017). Hydrothermal rutile indicates a mineralization age of 42.11  $\pm$  0.50 Ma, overlapping with the ages for the K, L porphyries and the latite dike as well as the <sup>40</sup>Ar/<sup>39</sup>Ar age of sericite (41.16  $\pm$  0.48 Ma; Gustafson et al., 2001) and Re-Os age of molybdenite (41.5  $\pm$  0.3 Ma; Zimmerman et al., 2014). Nevertheless, the better agreement of the average rutile age with field relationships suggests that it might be the best approximation for the mineralization age so far at El Salvador. Like for Bingham Canyon, the slightly younger molybdenite ages might be the result of two temporally separated precipitation events.

At Northparkes, the age of mineralization is not precisely constrained. It occurred within a ca. 16 Ma time span bracketed by U-Pb zircon SHRIMP dating of the pre-mineralization biotite quartz monzonite pluton (444.2 ± 4.7 Ma) and the post-mineralization zero porphyries (436.7 ± 3.3 Ma; Lickfold et al., 2007). This age can be refined to be in the 449-438 Ma range, defined by  $^{40}$ Ar/ $^{39}$ Ar dating of biotite in the syn-mineralization biotite QMP, both igneous (446.5 ± 2.6 Ma) and hydrothermal associated with potassic alteration (441.3 ± 3.8 Ma; Lickfold et al., 2007); as well as hydrothermal sericite (439.2 ± 1.2 Ma; Perkins et al., 1990). Most recently, Rb-Sr dating of epidote has been applied to propylitic alteration at the Northparkes deposits (Pacey et al., 2019) but the obtained age of 450 ± 11 Ma does not refine the age of hydrothermal activity. The U-Pb age of 442.22 ± 4.78 Ma obtained here for hydrothermal rutile overlaps within uncertainty with the previously best constrained time span for mineralization (defined by  $^{40}$ Ar/ $^{39}$ Ar dating) and narrows this span down to <10 Ma.

### 5.3. Advantages of U-Pb Rutile Dating in Porphyry Systems

Hydrothermal rutile from porphyry Cu deposits contains enough U, and consequently radiogenic Pb, for a good analytical precision on measured isotope ratios. With the exclusion of Batu Hijau (low U-, young rutile), analytical uncertainties on crystallization dates are <1% relative. When propagated uncertainties on rutile U-Pb ages are taken into account (see Methods for details), the final uncertainties range from 1.1 to 1.3% relative (excluding Batu Hijau). External uncertainties  $\ge 1\%$  are also expected for the Re-Os and  $^{40}$ Ar/ $^{39}$ Ar dating methods (Chiaradia et al., 2013), indicating that U-Pb dating of rutile can be as or more precise than the other isotope systems.

For grains with radii > 20  $\mu$ m and expected lifetimes of hydrothermal systems of < 1 Ma, closure temperatures for U-Pb in rutile are expected to be > 600°C (Cherniak, 2000; Vry and Baker, 2006). The breakdown of biotite in hydrothermal systems, and hence rutile formation, typically occurs at

considerably lower temperatures (< 450°C, e.g., Parry and Downey, 1982; Eggleton and Banfield, 1985). Therefore, the U-Pb system should not be affected by Pb diffusion, as indicated by the well-defined regressions for all four deposits (Fig. 5). The closing temperature of the <sup>40</sup>Ar/<sup>39</sup>Ar system within the same conditions is lower than for U-Pb in rutile, in the order of 350° and 300°C for muscovite and biotite, respectively (Dodson, 1973; Hames and Bowring, 1994). Partial or complete resetting by later thermal events, such as post-mineralization intrusions, is therefore more likely.

The Re-Os system in molybdenite has a closure temperature as high as rutile (Suzuki et al., 1996), and yields precise ages of molybdenite formation (e.g., Zimmerman et al., 2014). In several cases however, Re-Os molybdenite dating yielded diachronous ages covering time spans of up to few million years. For the Escondida and El Teniente porphyry Cu-Mo deposits for example, molybdenite dates cover an interval of 3 m.y. (Padilla-Garza et al., 2004; Romero et al., 2010) and 2 m.y. (Maksaev et al., 2004), respectively. From individual porphyry Cu-Mo systems in Northern Mexico Re-Os molybdenite geochronology also spans variable time intervals from < 2 m.y. up to 7 m.y. (Barra et al., 2005). The relative timing between Cu(-Au) and Mo mineralization in porphyry systems is not always clear (e.g., Seo et al., 2012; Spencer et al., 2015) and consequently Re-Os ages of molybdenite, despite being accurate and reliable, do not necessarily determine the age of Cu mineralization. At Bingham Canyon for instance, molybdenite Re-Os ages are significantly younger than our rutile U-Pb ages (Fig. 5).

Zircon geochronology by CA-ID-TIMS has been commonly used to determine the maximal duration of hydrothermal activity associated with porphyry intrusions (e.g., von Quadt et al., 2011; Buret et al., 2016; Large, 2018). However, zircon crystallized in the parental magma chamber before or during porphyry emplacement and is hence not temporally related to ore formation. Therefore, only bracketing of hydrothermal activity using the porphyry intrusions as time markers is possible. Moreover, it relies on the assumption that the youngest of the few dated zircon grains within a porphyry sample represents porphyry emplacement; and that individually dated grains are not zoned in age since dissolution of the whole zircon grain is necessary for ID-TIMS analysis. Despite the lower absolute analytical precision of the LA-ICP-MS technique compared to CA-ID-TIMS, rutile dating has the advantage of directly yielding the mineralization age. As a result, the maximum time periods of mineralization obtained by zircon CA-ID-TIMS at Bingham Canyon and Batu Hijau (respectively 662 and 122 ka; Large, 2018; Large et al., 2020) are only 1.5 to 3 times smaller than those obtained based on the uncertainties of our rutile LA-ICP-MS U-Pb dating (respectively 980 and 400 ka). Consequently, texturally controlled U-Pb analyses of hydrothermal rutile with LA-ICP-MS provide a new, accurate way to date porphyry-style Cu mineralization with less sample preparation, lower costs and easier accessible analytical setup than more time- and resource-demanding methods. For resolving the entire time scale of magmatic-hydrothermal processes in porphyry Cu deposits from high to low temperatures, a combination of U-Pb, Re-Os and <sup>40</sup>Ar/<sup>39</sup>Ar methods applied to various minerals is required. Rutile dating thereby complements the current geochronological toolbox for porphyry systems and might be the best option to rapidly and directly date Cu mineralization, provided that petrographic observations confirm co-formation of rutile and Cu-Fe sulfides.

Using direct CA-ID-TIMS dating of rutile, which would require inclusion-free and in the best-case common lead-free crystals, would allow for even more accurate and precise dating of hydrothermal activity in porphyry systems. In theory, the time gap between high-temperature mineralization associated with potassic alteration and hence rutile formation by titanite breakdown and low-temperature mineralization during biotite-destructive alteration, might be resolvable in future by dating the different rutile generations. Likewise, combining magmatic zircon and hydrothermal rutile U-Pb dating might provide further insights into the duration of porphyry ore formation, especially if the age relationships of different porphyry intrusions are absent or difficult to establish.

#### 5.4. Parameters Controlling Trace Element Variability of Rutile in Porphyry Cu Deposits

In the following subsections, the trace element contents of non- and hydrothermally formed rutile in general are firstly compared to each other to investigate the general effects of a fluid phase on the trace elemental composition of rutile. Subsequently, differences and similarities between the studied porphyry Cu deposits regarding rutile composition and its potential implications for mineralization conditions will be discussed. Our analytical work was focused on hydrothermal blocky rutile grains of the third generation, i.e., the ones formed contemporaneously with Cu-Fe sulfides during biotitedestructive alteration. Importantly, in a given deposit, we did not find any significant difference in trace element composition (and U-Pb age) between rutile directly associated with other alteration products of Ti-rich phases (e.g., chlorite or sericite) and rutile enclosed in dull-luminescent quartz. This may indicate that the latter represent crystals that were physically transported in the fluid from their site of formation in the host rock.

#### 5.4.1. Comparison of hydrothermal and non-hydrothermal rutile

Rutile is an accessory mineral in many metamorphic rocks, particularly in high-temperature and high-pressure metapelites, whereas igneous rocks rarely contain rutile (Zack et al., 2002). Siliciclastic rocks typically also contain abundant detrital rutile (Force, 1980; Morton and Hallsworth, 1994). Our dataset contains 650 LA-ICP-MS trace element analyses of rutile grains from Batu Hijau, Bingham Canyon, El Salvador, and Northparkes, which are compared with 1550 trace element analyses obtained by EMPA and LA-ICP-MS of non-hydrothermal rutile from pegmatite (Pe-Piper et al., 2019), various metamorphic rocks (Luvizotto and Zack, 2009; Meyer et al., 2011; Ewing et al., 2013; Gao et al., 2014; Sengün and Zack, 2016; Hart et al., 2018; Plavsa et al., 2018), highly fractionated igneous rocks from the Bushveld Complex (Ver Hoeve et al., 2018), and detrital rutile (Zack et al., 2004; Okay et al., 2011; Rösel et al., 2019). We also compare our results with rutile data from orogenic Au deposits (Agangi et

al., 2019) and topaz-bearing quartz veins (Santos et al., 2020). The comparison could only be based on the limited number of elements common to all these studies.

Combination of our dataset with rutile data from these various geological settings shows that generally hydrothermal and non-hydrothermal rutile can be distinguished based on differences in their trace element characteristics (Fig. 11). Elements like Fe, Sn, W and potentially Si are more enriched in hydrothermally formed rutile, whereas concentrations of other elements like Mo and V are not systematically different (Fig. 9B and 11E). Elements considered to be fluid immobile like Nb, Zr, and Cr do not appear to be considerably depleted in hydrothermal rutile (Fig. 9). Rutile from the investigated porphyry Cu deposits is distinct from non-hydrothermal rutile regarding their high Sn and W contents, their low V and Cr concentrations relative to Fe and the generally large compositional variations, even within individual deposits, compared to more uniform concentrations in rutile from metamorphic environments (Fig. 12). This suggests that the chemical composition of hydrothermal rutile is influenced by multiple factors, most importantly the fluid composition and the nature of precursor minerals (e.g., Rabbia and Hernandez, 2012), whereas the composition of non-hydrothermal rutile is well-equilibrated with its host rock by protracted residence at high temperature (e.g., Zack et al., 2004; Watson et al., 2006; Tomkins et al., 2007). Elemental compositions of detrital rutile grains generally overlap with those of metamorphic rutile but span wider ranges (Fig. 9 and 12) due to their different origins, potentially including hydrothermal systems.

In addition, the composition of rutile from porphyry Cu deposits and non-hydrothermal rutile define distinctive trends in Fe/V vs. V and Fe/Cr vs. Cr diagrams (Fig. 12B and C). The former show higher V concentrations at a given Fe/V ratio; and lower Cr contents and conversely higher Fe/Cr ratios, except Bingham Canyon that shows similar Fe/Cr ratios as non-hydrothermal rutile yet at higher Cr contents (Fig. 12 B and C). Although elevated V concentrations in rutile from mineralized samples at Northparkes (> 0.4 wt.%) were already reported by Scott (2005) and agree with our analytical results (e.g., Fig. 9B and 12B), extreme V enrichment (up to 6.3 wt.%) as reported from the Pebble porphyry Cu deposit (Kelley et al., 2010) appears not to be characteristic for porphyry systems in general. Contrary, most rutile grains from the investigated porphyry Cu deposits overlap with those from metamorphic or sedimentary environments regarding their V concentrations (Fig. 9B and 12B), indicating that hydrothermal processes do not significantly affect total V concentrations in rutile.

Rutile formed in other hydrothermal environments show similarly elevated Si, Fe, Sn, and W concentrations as porphyry Cu rutile (Fig. 11). A major compositional difference is visible in rutile from orogenic Au systems, which is strongly enriched in As and/or Sb (Agangi et al., 2019) relative to porphyry Cu rutile (Fig. 13). This emphasizes the influence of the fluid chemistry on rutile composition, as fluids forming orogenic Au deposits are assumed to be rich in As and Sb (Phillips and Powell, 2010; Goldfarb and Groves, 2015). Although high Sb concentrations in rutile have been frequently reported

from Au-rich hydrothermal systems (e.g., Smith and Perseil, 1997; Clark and Williams Jones, 2004; Porter et al., 2020), Sb and As concentrations in rutile from all four porphyry systems significantly overlap with each other (Fig. 13), irrespective of their metal endowment.

#### 5.4.2. Inherited trace element signatures in rutile from porphyry systems

Fluid immobile elements such as Zr, Ta, Nb, V and Cr are not systematically depleted in hydrothermal rutile compared to igneous and metamorphic rutile (Fig. 9 and 12), highlighting the importance of inherited trace element signatures from the host rocks and its minerals, particularly biotite.

Rutile from Batu Hijau generally contains lower concentrations of V, Nb, Ta, Zr, Hf, Mo and U compared to the other deposits (Fig. 8A and 9). This might reflect the petrogenesis of the associated tonalitic melts in an intra-oceanic arc system, formed by melting of asthenospheric mantle with only limited subsequent assimilation of crustal material (Fiorentini and Garwin, 2010). This could explain the generally lower contents of incompatible elements in rutile from Batu Hijau compared to the other porphyry deposits, which are situated in continental arc systems where assimilation of crustal crust is more likely.

Conversely, rutile from Bingham Canyon is considerably richer in Nb, Ta and Cr compared to rutile from the other deposits, indicating that precursor biotite might have been also enriched in these elements. Partitioning experiments suggest that mica/melt partition coefficients for Nb and Ta are strongly correlated to each other (Ewart and Griffin, 1994; Acosta-Vigil et al., 2010) and to the TiO<sub>2</sub> content of biotite (Stepanov and Hermann, 2013). Biotite from Bingham Canyon contains high TiO<sub>2</sub> contents of up to 6 wt.% (Moore and Czamanske, 1973), implying high Nb and Ta concentrations. The high Cr contents (> 1000  $\mu$ g/g) in rutile from Bingham Canyon are probably also inherited from precursor biotite, possibly reflecting the involvement of more mafic magmas that are described at Bingham Canyon as mafic inclusions and dikes with high Cr contents (Keith et al., 1998; Maughan et al., 2002; Redmond and Einaudi, 2010).

On top of these first-order differences related to host rock petrogenesis and mineral composition, different degrees of biotite replacement would explain the observed ranges of fluid-immobile trace element contents in rutile from all deposits. The high HFSE compatibility in rutile (Klemme et al., 2005), which is probably higher than in biotite as demonstrated for Nb (Luvizotto and Zack, 2009), causes the first formed rutile grains to incorporate high amounts of HFSE, while the residual biotite becomes more and more depleted in those elements with progressive replacement (cf., Luvizotto and Zack, 2009). Accordingly, rutile grains formed from already HFSE-depleted biotite contain progressively lower concentrations of those elements, explaining the large elemental variations (Fig. 9). The same might apply for the variations of Mo and U in hydrothermal rutile, which both correlate positively with Zr (Fig. 8B, 9D and F), as all of them are tetravalent with comparable ionic radii. Likewise, Mo contents of

rutile might be mainly inherited from Ti-rich precursor phases (e.g., Rabbia et al., 2009) as they do not correlate with Mo grades in the porphyry deposits. For example, rutile Mo concentrations are comparable at Northparkes, a Cu-Au porphyry not particularly enriched in Mo, and at Bingham Canyon and El Salvador, both mined for Mo in addition to Cu. Rabbia et al. (2009) reported similar Mo concentrations from the El Teniente porphyry Cu-Mo deposit.

#### 5.4.3. Fluid-derived trace element variations in rutile from porphyry systems

Compared to most other elements, Fe contents of hydrothermal rutile are less variable within each of and across the four porphyry Cu deposits (Fig. 9E). Iron has been shown to be predominantly incorporated into rutile as Fe<sup>3+</sup> (Murad et al., 1995; Bromiley et al., 2004), via coupled substitutions like  $Fe^{3+} + Nb^{5+} \leftrightarrow 2Ti^{4+}$  (Bromiley and Hilairet, 2005), resulting in positive correlations between  $Fe^{3+}$ and other trivalent and pentavalent cations. However, no direct correlation between Fe and Nb or Ta concentrations can be observed in the investigated deposits (Fig. 9E). When comparing molar amounts of potentially trivalent and penta- and hexavalent cations, coupled substitutions should be identifiable by linear trends defined by the respective substitution mechanism (e.g., Scott et al., 2011; Carocci et al., 2018). Rutile from the investigated porphyry Cu deposits contains significantly higher amounts of trivalent cations compared to penta- and hexavalent cations than expected considering typical coupled substitutions, particularly when V is assumed to be present as trivalent cation (Fig. 15A). Without V, there is a better agreement between analyzed rutile compositions and the linear relationships defined by potential coupled substitutions but many rutile grains, particularly from Batu Hijau, still contain too high amounts of trivalent cations (Fig. 15B). Considering all V being present in the pentavalent state, most rutile compositions overlap with the three shown coupled substitution possibilities, although there is still an excess of trivalent cations in many rutile grains from Batu Hijau (Fig. 15C). This indicates that V in rutile from porphyry Cu systems may be present as a mixture of tetravalent and pentavalent cations, which would also explain the correlations with variable elements such as Sb and Sn (Fig. 8). At Batu Hijau and Bingham Canyon, V is positively correlated with Sb (Fig. 8C and D), suggesting that both elements are introduced into rutile via similar substitutions and hence a considerable portion of V may be present in its highly oxidized form. At El Salvador and Northparkes in contrast, V shows a rather negative correlation with Sb indicating that both elements are part of competing substitution mechanisms and hence V<sup>4+</sup>, which can directly replace Ti<sup>4+</sup>, is the dominant oxidation state of V. In addition, oxygen-vacancies can charge-balance the incorporation of trivalent cations, implying a strong influence of f(O<sub>2</sub>) on Fe concentrations in rutile (Bromiley and Hilairet, 2005; Meinhold, 2010). High Fe concentrations in rutile from all deposits and the presence of tetra- and pentavalent V point towards high oxygen fugacities during biotite-destructive alteration in the porphyry systems, which is further supported by the presence of texturally associated anhydrite (Fig. 3).

The influence of the fluid phase on rutile geochemistry is particularly well visible in the form of noncharge-and-radius-controlled ("CHARAC"; Bau, 1996) behavior in element ratios and the chondrite normalized REE + Y patterns (Fig. 10B). Concentrations of Zr and Hf as well as Y and Ho are tightly coupled to each other but their ratios diverge from chondritic values (37.1 and 28.75, respectively, McDonough and Sun, 1995). Such elements of nearly identical charge and radii can only be fractionated by hydrothermal processes because they form different complexes in aqueous solutions (Bau and Dulski, 1995; Bau, 1996). Subchondritic Zr/Hf and Y/Ho ratios (and corresponding negative Y anomaly; Fig. 10B), as well as generally lower Zr contents of hydrothermal vs. non-hydrothermal rutile, suggest that the solubilities of Zr and Y in the hydrothermal solution were lower than those of Hf and Ho. Although both REE and Y form complexes with F (e.g., Bau and Dulski, 1995), REE rather form monofluoride complexes (Migdisov et al., 2009) whereas Y preferentially occurs as di-fluoride complex, so that their relative solubility is strongly correlated to fluorine activity in the fluid (Loges et al., 2013). The mobility of Zr in hydrothermal solutions is also enhanced by the presence of F (Rubin et al., 1993; Gysi and Williams-Jones, 2013). Consequently, limited but sufficient quantities of F in the hydrothermal fluid might have been favorable for the stabilization of aqueous complexes of Y and Zr over those of REEs. Moreover, elevated Hf and REE concentrations in rutile agree with experimentally determined high partitioning coefficients between rutile and fluid (Brenan et al., 1994).

Due to the non-CHARAC behavior of element partitioning in hydrothermal rutile and the lack of equilibrium with zircon, the Zr-in-rutile thermometer (Zack et al., 2004; Watson et al., 2006; Ferry and Watson, 2007) is not applicable to hydrothermal rutile (cf., Cabral et al., 2015). Other potential thermometers based on Si and Al in rutile (e.g., Ren et al., 2009; Hoff and Watson, 2018) have not been calibrated yet for hydrothermal temperature and pressure conditions but might be applicable to hydrothermal rutile in the future.

#### 5.5. Rutile as Exploration Tool for Porphyry Cu Systems

Hydrothermal rutile occurs in various ore deposit types, including Carlin-type Au, sediment-hosted stratiform Cu, VMS, orogenic Au, quartz-vein type W-Sn, IOCG, and porphyry Cu deposits (Richards et al., 1988; Schandl et al., 1990; Clark and Williams-Jones, 2004; Rabbia et al., 2009; Pi et al., 2017; Carocci et al., 2018; Agangi et al., 2019). During erosion, rutile becomes concentrated by sedimentary processes as consequence of its high density, resistance to weathering and transport (Force, 1980). Cox (1986) noted that soils above mineral deposits contain anomalous rutile concentrations. Consequently, numerous studies have focused on the utilization of rutile as pathfinder for mineralization (e.g., Williams and Cesborn, 1977; Force et al., 1984; Clark and Williams-Jones, 2004; Scott, 2005; Scott and Radford, 2007; Scott et al., 2011; Kelley et al., 2011; Carocci et al., 2018; Plavsa et al., 2018; Plouffe et al., 2018; Agangi et al., 2019; Porter et al., 2020).

So far, investigations of rutile from porphyry Cu deposits were mainly qualitative (focused on distribution, crystal color and shape; Williams and Cesborn, 1977; Force et al., 1984; Plouffe et al., 2018). As discussed earlier, discrimination of hydrothermal, including rutile formed in porphyry systems, and non-hydrothermal ("background") rutile is possible (Carocci et al., 2018; Plavsa et al., 2018; Agangi et al., 2019; Porter et al., 2020). Rutile from porphyry systems is systematically enriched in Si, Fe, Sn, and W compared to "background" rutile (Fig. 11, 12A). Concentrations of Sn and W higher than 100 and 500  $\mu$ g/g, respectively, occur in approximately 75% of the rutile grains from porphyry systems but are uncommon in "background" rutile (Fig. 12A). Such criteria might be used to identify hydrothermal rutile in detrital datasets. For instance, the dataset of Rösel et al. (2019), who concluded that part of the studied detrital material originated from magmatic rocks of the Cadomian arc system, contains rutile displaying high concentrations of Sn, W and Fe, indicating that hydrothermal rutile might be present. Significant V enrichment, which has been described from some porphyry systems (e.g., Scott, 2005; Kelley et al., 2010) has not been found in our dataset (Fig. 12B). Although some rutile grains from the Nortparkes sample show high V contents of up to 1 wt.%, which is comparable with the data reported by Scott (2005), a systematic enrichment of V in hydrothermal compared to nonhydrothermal rutile seems not to be a general feature of porphyry systems. The spatial variations of V within an individual porphyry system as mentioned by Scott (2005) could not be investigated based on the limited sample material studied from each deposit. Distinctively high Fe concentrations in rutile from porphyry systems result in the relatively steep trends shown for Fe/Cr vs. Cr and Fe/V vs. V when compared to "background" rutile (Fig. 12B and C). Rutile of metamorphic origin is assumed to preserve Cr and V bulk rock characteristics (e.g., Meyer et al., 2011) resulting in less variable Cr and V contents, compared to rutile from porphyry Cu deposits, and in combination with their lower Fe concentrations leads to Fe/Cr vs. Cr and Fe/V vs. V trends that are less steep, making a distinction of metamorphic and hydrothermal rutile possible (Fig. 12). Finally, other elements analyzed here, like Mn, Cu, Zn, Ag, Se, Te, Hg and REE, might be useful for distinguishing rutile associated with porphyry Cu systems, but this could not be assessed because they were not systematically analyzed in other studies.

Besides trace element signatures, the presence, abundance and type of fluid inclusions might be important criteria for distinction of rutile from different settings. Rutile from porphyry systems studied here commonly contains aqueous fluid inclusions consisting of a small bubble (< 30 vol.%) surrounded by liquid (Fig. 4). In contrast, well-preserved fluid inclusions in metamorphic rutile are comparatively rare and typically rich in  $CO_2$  (e.g., Ni et al., 2008; Cabral et al., 2015).

#### 6. Conclusions and outlook

Hydrothermal rutile forms throughout the hydrothermal evolution of a porphyry system and contains several layers of information, including the absolute timing of Cu-sulfide mineralization, insights into magmatic and hydrothermal processes, fluid composition and mineralizing conditions. Its

trace element composition can furthermore be used as pathfinder for hydrothermal activity, which might be related to economic metal accumulation. Specifically, comparison of trace element signatures from hydrothermal and "background" rutile emphasizes its promising potential as pathfinder for blind ore deposits in highly eroded terranes, where the use of rutile as exploration tool was already investigated (e.g., Scott, 2005; Kelly et al., 2010). Different types of ore deposits, like orogenic Au and porphyry Cu, can be clearly distinguished based on rutile geochemistry, which provides additional insights into hydrothermal fluid compositions responsible for different mineralization styles. However, in order to certify rutile as exploration tool, more trace element data from non-hydrothermal rutile including a broader range of elements is needed.

We have obtained LA-ICP-MS U-Pb ages for rutile formation that overlaps in time with Cu mineralization, for the four studied porphyry deposits. Comparison with existing high-precision CA-ID-TIMS data for two of these (Batu Hijau, Bingham Canyon) ascertained the accuracy of our results, and application to two less well dated systems (El Salvador, Northparkes) yielded precise constraints on mineralization ages (ca. 1.1 to 1.3% relative). Using TIMS for dating inclusion-free unzoned rutile grains with low common Pb contents would result in smaller uncertainties, which could open up new possibilities for determining timescales of mineralization in porphyry systems, especially when combined with high-precision zircon dating.

Almost completely unexplored are fluid inclusions hosted in hydrothermal rutile. Fluid inclusions bigger than around 5 µm are not uncommon in hydrothermal rutile and sufficiently large for microthermometric measurements, whereas fluid inclusions with sizes suitable for LA-ICP-MS analysis are rare but not absent in rutile from the investigated porphyry systems. Rutile-hosted fluid inclusions might be less prone to post-entrapment modifications compared to quartz, in which small monovalent cations like Li, Cu, and Ag can diffuse through the quartz lattice distorting the original fluid composition (e.g., Zajacz et al., 2009; Lerchbaumer and Audétat, 2012; Seo and Heinrich, 2013). Consequently, rutile also bears potential for future fluid inclusion microanalysis to further constrain the fluid evolution of porphyry systems.

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Fig. 1: Rutile petrography identifying different textural positions of rutile and mineral associations in Batu Hijau, Bingham Canyon, El Salvador, and Northparkes. A) Transmitted light image (PPL/XPL) of blocky, hydrothermal rutile in chlorite-sericite altered rock from Batu Hijau. Rutile grains are in contact with bornite grain and mantled by chlorite. The small inset show a reflected light image of the two rutile grains and bornite. The small cavity shows a negative crystal shape, possibly representing a breached rutile-hosted fluid inclusion (sample 267-757). B) and C) Transmitted (PPL/XPL) and reflected light images, respectively, showing intergrowth of elongated hydrothermal rutile with chalcopyrite in chlorite-sericite altered rock from Batu Hijau (sample 257-694). D) Transmitted light image of a thick section from Bingham Canyon showing two generations of rutile, needle-like exsolutions (sagenetic texture) and blocky rutile, in biotite phenocryst, partially replaced by sericite (sample 195-991). E) Sericite replacing biotite in the presence of chalcopyrite in Bingham Canyon, producing numerous blocky rutile grains with sizes typically < 25 µm (sample 123-210). F) BSE image of complex zoned anhedral rutile with apatite inclusion associated with partial replacement of biotite by chlorite from El Salvador. Brighter zones are characterized by elevated Si and Fe contents (sample 946-315). G) Combined transmitted and reflected light image showing rutile and chalcopyrite associated with chlorite within a paint vein that crosscuts an earlier quartz vein at El Salvador (sample 1104-4.3). H) Combined transmitted and reflected light image of blocky rutile in chlorite, El Salvador (sample 946-315). I) Combined transmitted and reflected light image of rutile, sericite, albite, and anhydrite intergrown with bornite in a K-feldspar – biotite matrix partially overprinted by later albite and sericite, Northparkes. J) BSE/reflected light image of rutile intergrown with bornite and chalcopyrite, Batu Hijau (sample 257-507). K) Rutile intergrown with and as inclusions in anhedral bornite filling open spaces between euhedral quartz crystals, Northparkes. L) Rutile cluster in chlorite – sericite altered rock from El Salvador. Note that rutile grains are cemented by calcic minerals such as anhydrite, calcite, and apatite in combination with sericite and K-feldspar. Chalcopyrite occurs in between rutile grains, partially surrounding them (sample 946-315). Abbreviations: Alb – albite, Anh – anhydrite, Ap – apatite, Bi – biotite, Bn – bornite, Ca- calcite, Chl – chlorite, Cpy – chalcopyrite, K-Fsp – K-feldspar, Olg – oligoclase, Qtz – quartz, Rt – rutile, Ser – sericite. (2-column, color)

Fig. 2: Phase map created with iSpectra (Liebske, 2015) showing textural relationship between rutile and other silicate alteration minerals (Bingham Canyon, sample 162-362). A) K-silicate alteration with sericitic overprint showing remnants of a primary biotite (bi) phenocryst partially overprinted by sericite (ser) in K-Feldspar (ksp) and quartz (qtz matrix). Accessory minerals are rutile (rt), apatite (ap), zircon (zr) and chalcopyrite (cpy). B) Enlarged section of A), emphasizing the spatial relationship between blocky rutile and biotite-replacing sericite. Using conventional transmitted light microscopy, this textural relationship can be less clear, especially if biotite-replacement is weakly developed, which gives the impression that some blocky rutile is hosted by secondary biotite. (single-column, color)

Fig. 3: Cathodoluminescence images supporting the association of rutile with Cu-Fe sulfides in the different porphyry systems. A) and B) CL and reflected light image, respectively, of euhedral quartz crystal growing into open space, Batu Hijau. Note that the partially resorbed bright-luminescent core does not contain any sulfide. Chalcopyrite occurs exclusively in the dull-luminescent rim together with blocky rutile and small anhydrite grains (sample 257-694). C) and D) CL and combined transmitted and reflected light image, respectively, of chalcopyrite and rutile hosted by a micro-fracture network filled with dull-luminescent quartz crosscutting earlier bright-luminescent quartz, Bingham Canyon (sample 123-210). E) and F) CL and BSE image of a paint vein containing chalcopyrite, rutile, chlorite, sericite, and anhydrite mantled by dull-luminescent quartz, crosscutting earlier bright-luminescent quartz, El Salvador (sample 946-315). G) and H) Bornite, rutile, anhydrite, and sericite hosted by a micro-fracture network filled with dull-luminescent quartz, rosscutting earlier bright-luminescent quartz, El Salvador (sample 946-315). G) and H) Bornite, rutile, anhydrite, and sericite hosted by a micro-fracture network filled with dull-luminescent quartz crosscutting earlier bright-luminescent quartz, El Salvador (sample 946-315). G) and H) Bornite, rutile, anhydrite, and sericite hosted by a micro-fracture network filled with dull-luminescent quartz crosscutting earlier bright-luminescent quartz, Northparkes. Abbreviations as in figure 1. (1.5-column, color)

Fig. 4: Transmitted light images of blocky rutile grains hosting aqueous fluid inclusions (AQ FIs). Selected fluid inclusions are enlarged to better illustrate phase proportions of the liquid (L) and vapor (V) phases, pointing towards relatively high fluid densities of approximately 0.7 to 0.8 g/cm<sup>3</sup>. Note the similarities to aqueous fluid inclusions hosted by (dull-luminescent) quartz in A). (2-column, color)

Fig. 5: Tera-Wasserburg diagrams of U-Pb rutile dating from Batu Hijau, Bingham Canyon, El Salvador, and Northparkes produced with IsoplotR (Vermeesch, 2018). The different colors represent different samples from the individual porphyry systems. Ages, analytical uncertainties (2 $\sigma$ ), and the MSWD is given for each individual sample in the respective color. The average age, analytical uncertainty (2 $\sigma$ ), and MSWD is given in black for each deposit. Note that ages reported for Batu Hijau are corrected for <sup>230</sup>Th/<sup>238</sup>U disequilibrium. Only one open pit sample was available from Northparkes. The insets in the upper right corners compare our rutile dates with available literature data: 1 – Large et al. (2020), U-Pb zircon CA-ID-TIMS dating; 2 – Garwin (2000), <sup>40</sup>Ar/<sup>39</sup>Ar hydrothermal biotite and sericite dating; 3 – Parry et al. (2001) U-Pb zircon SHRIMP and <sup>40</sup>Ar/<sup>39</sup>Ar hydrothermal biotite dating, 4 – Large (2018), U-Pb zircon CA-ID-TIMS dating; 5 – Chesley et al. (1997), Re-Os molybdenite dating; 46 – Lee et al. (2017), U-Pb zircon SHRIMP dating; 7 – Gustafson et al. (2001), <sup>40</sup>Ar/<sup>39</sup>Ar sericite dating; 8 – Zimmerman et al. (2014), Re-Os molybdenite dating; 9 – Lickfold et al. (2007), U-Pb zircon SHRIMP dating; 10 – Lickfold et al. (2003), <sup>40</sup>Ar/<sup>39</sup>Ar igneous and hydrothermal biotite dating. See text for abbreviations. (2-column, color)

Fig. 6: Trace element indications for contaminated LA-ICP-MS analyses of rutile. The good correlation between Si and Al as well as extremely high Si contents observed in some rutile analyses indicate contamination with other silicates such as quartz and feldspars due to the relatively small grain sizes and complex intergrowth texture of rutile with other minerals. Another source of contamination is given by frequent mineral and fluid inclusions as shown by the positive correlation of Zn and Cu with Na. Insets are transmitted light microscope images of aqueous fluid inclusions in rutile. (2-column, color)

Fig. 7: Time-integrated LA-ICP-MS signals of rutile containing fluid and mineral inclusions, respectively. Unfortunately, P was not included in our element list, but we assume that the REE-rich mineral inclusions encountered during LA-ICP-MS analysis are most likely monazite close to the Ce-dominant endmember. (2-column, color)

Fig. 8: Principal component analysis (PCA) of blocky rutile from porphyry Cu deposits. A) Scores from the first two principal components of rutile from all porphyry deposits with colors and symbols representing the individual deposits. B) Loadings of each element of the first two principal components accounting for 63.94% of trace element variability in rutile from all porphyry deposits. C) to F) Loadings of each element of the first two principal components from each individual porphyry Cu deposit. (2-column, color)

Fig. 9: Selected trace element compositions of rutile from Batu Hijau, Bingham Canyon, El Salvador, and Northparkes. Background shades indicate the compositional ranges of rutile from metamorphic and sedimentary environments reported in the literature (Zack et al., 2004; Luvizotto and Zack, 2009; Meyer et al., 2011; Okay et al., 2012; Ewing et al., 2013; Gao et al., 2014; Sengün and Zack, 2016; Hart et al., 2018; Plavsa et al., 2018; Rösel et al., 2019). (2-column, color)

Fig. 10: REE + Y spider diagram normalized against C1 chondrite (McDonough and Sun, 1995) and Zr/Hf vs Y/Ho ratios of hydrothermal rutile from Batu Hijau, Bingham Canyon, El Salvador, and Northparkes. CHARAC-field after Bau (1996), Y/Ho and Zr/Hf ratios of chondrite from Anders and Grevesse (1989). (single-column, color)

Fig. 11: Box and Whisker plot for comparison of selected trace elements from hydrothermal and nonhydrothermal rutile. Rutile from porphyry deposits are from this study, whereas other hydrothermal rutile are from numerous orogenic Au deposits (Agangi et al., 2019) and imperial topaz-bearing quartz (± calcite) veins from Brasil (Santos et al., 2020). Non-hydrothermal rutile includes rutile from pegmatite (Pe-Piper et al., 2019), the Bushveld pluton (Ver Hoeve et al., 2018), various metamorphic environments (Luvizotto and Zack, 2009; Meyer et al., 2011; Ewing et al., 2013; Gao et al., 2014; Sengün and Zack, 2016; Hart et al., 2018; Plavsa et al., 2018) and detrital rutile (Zack et al., 2004; Okay et al., 2012; Rösel et al., 2019). Missing boxes indicate that the respective trace element was not included in the element setup of the individual studies, which hampers comparison of rutile data to some extent. For example, Pe-Piper et al. (2019) did not measure Fe in rutile from pegmatites and Ver Hoeve et al. (2018) did not include Sn in their measurements of igneous rutile from the Bushveld complex. (2-column, color)

Fig. 12: Comparison of selected trace elements and ratios of rutile from Batu Hijau, Bingham Canyon, El Salvador, and Northparkes with "background" rutile. References for "background" rutile are the same as in Figure 8 and given in the text. The box plots on the opposite side of the axes show the overall range of elemental concentrations with the same color-coding as used in Figure 8. As shown in the uppermost diagram, the highest enriched elements in hydrothermal compared to "background" rutile are Sn and W, which clearly distinguish hydrothermal rutile from porphyry systems from metamorphic and detrital rutile. The partial overlap of detrital and hydrothermal rutile might be due to the presence of hydrothermally formed rutile in the analyzed detritus. Vanadium and Cr are not particularly different in rutile from porphyry systems but show steeper correlations with Fe/V and Fe/Cr, respectively, representing the generally enriched Fe contents in hydrothermal rutile. The ellipses in the lower two diagrams are 95% confidence robust ellipses calculated with IoGAS. (1.5-column, color)

Fig. 13: Difference between rutile from porphyry Cu deposits and orogenic Au deposits, which can be clearly separated based on the high Sb and As contents of rutile from orogenic Au deposits. Data for orogenic Au deposits from Agangi et al. (2019) and includes rutile from mineralized samples from Fortnum, Killara and Nathans (Capricorn Orogen, Australia), Sheba and Fairview (Baberton Greenstone Belt, South Africa), and Obuasi (Ashanti Belt, Western Africa). Ellipses contain 95% of the data points of the respective rutile groups and were calculated with IoGas. (2-column, color)

Fig. 14: Sketch showing formation of the different rutile generation during the evolution of the various alteration zones in mineralized porphyry Cu systems. Note that chlorite might not necessarily be present in all parts of a given deposit as its formation depends on host rock and fluid composition but is shown here to represent biotite-destructive alteration in general. In cases where chlorite is not present, sericite is the main alteration product replacing primary and secondary biotite. (2-column, color)

Fig. 15: Comparison of hydrothermal trace element composition of rutile from porphyry deposit with linear relationships between di-, tri-, penta- and hexavalent elements indicative for coupled substitution mechanisms represented by grey lines with slopes of 2, 1 and 0.5. M represents Nb<sup>5+</sup>, Ta<sup>5+</sup>, Sb<sup>5+</sup> and V<sup>5+</sup> or W<sup>6+</sup>, N can be Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> and V<sup>3+</sup> and P represents divalent cations such as Fe<sup>2+</sup>. (1 column, color)