

Revision 1

Incorporation mechanism of tungsten in W-Fe-Cr-V-bearing rutile

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Abstract – Rutile is a common mineral in many types of ore deposits and can carry chemical or isotopic information about the ore formation. For closer understanding of this information, the mechanisms of incorporation of minor elements should be known. In this work, we have investigated natural rutile crystals with elevated concentration of WO₃ (up to 17.7 wt.%), Cr₂O_{3,tot} (7.5), V₂O_{3,tot} (4.1), FeO_{tot} (7.3), and other metals. X-ray absorption spectroscopy (XAS) on rutile on the Fe K, Cr K, V K, and W L₁ and L₃ edges shows that all cations are coordinated octahedrally. The average oxidation state of V is +3.8, that of Cr near +4. Shell-by-shell fitting of the W L₃ EXAFS data show that W resides in the rutile structure. Raman spectroscopy excluded the possibility of hydrogen as a charge-compensating species. High-resolution TEM and electron diffraction confirm this conclusion as the entire inspected area consists of rutile single crystal with variable amount of metals other than Ti. Our results show that rutile or its precursors can be efficient vehicles for tungsten in sedimentary rocks, leading to their enrichment in W and possibly later fertility

25 with respect to igneous ore deposits. Leucoxene, a nanocrystalline mixture of Ti and Fe
26 oxides, is an especially suitable candidate for such a vehicle.

27 Key words: rutile, tungsten, incorporation, X-ray absorption spectroscopy, transmission
28 electron microscopy, ore deposits

29 Introduction

30 Rutile and cassiterite are common minerals in many types of ore deposits, for example,
31 greisen-type deposits (e.g., Moscati and Neymark 2020). Their trace element and isotopic
32 composition carries much information about the ore-forming processes, and, therefore,
33 cassiterite has been called the ‘zircon of hydrothermal systems’ (Blevin and Norman 2010),
34 although this term could be equally well applied to rutile. The degree to which we can
35 understand this information depends not only on detailed studies of selected ore deposits,
36 but also on the knowledge of how are these elements associated with the host mineral,
37 what is their chemical and oxidation state, and how do they partition between co-existing
38 minerals. The mode of association could bring additional insights into the processes that
39 form ore deposits.

40 An element that is increasingly reported in elevated concentrations in rutile or cassiterite
41 is tungsten (e.g., Kwak 1983, Rice et al. 1998, Clark and Williams-Jones 2004, Müller and
42 Halls 2005, Novák et al. 2008, Mozola et al. 2017; Reznitsky et al. 2017; Moscati and
43 Neymark 2020; Bennett et al. 2020). The ore deposits of tungsten are commonly linked to
44 acidic or intermediate igneous complexes but not all such complexes, no matter how
45 evolved, develop an ore deposit, a camp of ore deposits, or even small ore occurrences (cf.
46 Fig. 2 in Romer and Kroner 2016). For tungsten, the source magmatic rocks have been
47 commonly assigned to reduced S-type granitic magmas of crustal origin (e.g. Yuan et al.
48 2018) but, as pointed out by Lecumberri-Sanchez et al. (2017), such magmatism alone is
49 insufficient to generate Sn-W deposits. These rocks must be fertile, with pre-magmatic,
50 elevated concentrations of W, Sn, and other elements (Romer and Kroner 2014, 2016).
51 Fortuitous enrichment of the protolith by metals – for example by weathering of older ore

52 deposits – could be an explanation in a few cases but would not apply to the majority of the
53 magmatic complexes. Furthermore, it would not solve the question of the metal enrichment
54 in the protolith but only shift it to geologically older formations.

55 In this work, we investigated the incorporation mechanisms of tungsten and associated
56 elements in rutile. Using electron microprobe analyses, X-ray absorption and Raman
57 spectroscopy, and transmission electron microscopy, the association of tungsten and other
58 elements and the host structure was determined on the scale of micro- to nanometers. This
59 information is then used to contemplate which minerals could transport and retain tungsten
60 in sediments.

61 Geological settings

62 The W-Mo deposit Ochtiná (eastern Slovakia) is hosted by weakly metamorphosed rocks
63 but is genetically linked to a hidden body of Cretaceous Rochovce I-type granite (Határ et al.
64 1989, Poller et al. 2001, Kohút et al. 2013). Pyrite is common and is usually the most
65 abundant opaque phase in the ores (Bendel 2017). Beside pyrite, the ores contain also
66 frequently chalcopyrite and magnetite. The most important carriers of W and Mo are
67 scheelite, minerals of the wolframite group, and molybdenite, respectively (Határ et al.
68 1989, Gargulák and Rojkovičová 1993, Slavkay et al. 2004). The country rocks contain also
69 dispersed ilmenite, titanite, apatite, and rare Mg phosphates (Bendel 2017).

70 The deposit is made of flat-lying zones in the exocontact of the granitic intrusion. The
71 upper zone, approximately 100 m thick, is particularly enriched in tungsten. This zone was
72 sampled by the diamond drill holes OV-1, OV-2, and OV-3 drilled by the company Green
73 View, Ltd. These drill holes were the sources of the samples for this study. The W contents
74 in the drill core range between 2 and 30,000 ppm; the more detailed information and

75 correlation of W concentrations with depth are proprietary data of Green View, Ltd. In this
76 work, we have specifically focused on drill-core sections with elevated W concentrations.
77 The lower exocontact zone, enriched in molybdenum, was not investigated.

78 Methods and materials

79 Hand pieces of the drill holes, selected on the basis of visual examination and chemical
80 analyses (for Ochtiná, proprietary data of Green View, Ltd.), visual observations in visible
81 and UV light, were prepared in a form of standard thin sections. The sections were
82 inspected in transmitted and reflected polarized light to identify the minerals and their
83 temporal relationships and to further narrow down the selection for electron microscopy
84 and X-ray spectroscopy.

85 After screening of 50 samples and the corresponding sections and extensive EMP work,
86 two thin sections were selected for further work. One was made from a sample taken in the
87 drill core OV-1, depth 37.8 m. It contained many rutile crystals; of these, the crystal labeled
88 "9" was chosen for detailed work. Another sample was made from drill core OV-3, depth
89 27.8 m, and a crystal "T" was taken for further work.

90 Electron microprobe (EMP) analyses of rutile and other minerals were acquired with a
91 JEOL JXA 8530FE electron microprobe, with accelerating voltage of 15 kV, current 20 nA,
92 counting time 20 s on the peak and 10 s in the background, beam diameter 1-3 μm . The
93 standards, and emission lines measured were: Ca ($K\alpha$), diopside; Sn ($L\alpha$), cassiterite; K ($K\alpha$),
94 orthoclase; Nb ($L\alpha$), LiNbO_3 ; W ($M\alpha$), scheelite; Ta ($M\alpha$), CrTa_2O_6 ; Mg ($K\alpha$), olivine; Al ($K\alpha$),
95 albite; Fe ($K\alpha$), hematite; Cr ($K\alpha$), Cr_2O_3 ; V ($K\alpha$), vanadinite; Ti ($K\alpha$), rutile; Sc ($K\alpha$), ScVO_4 ; Mn
96 ($K\alpha$), rhodonite. The estimated detection limits (DL) were 0.01 weight % for most elements,
97 with the exception of W and Ta with estimated DL of 0.02 weight %.

98 For the micro-X-ray fluorescence (μ -XRF) and X-ray absorption (μ -XAS) measurements,
99 the glass slides of the thin sections were manually ground and polished down so that the
100 total thickness of the section was $\approx 100 \mu\text{m}$. The data were collected at the beamline of the
101 Synchrotron Radiation Laboratory for Environmental Studies (SUL-X,) in the synchrotron
102 radiation source of the Karlsruhe Institute of Technology (Germany). A silicon (111) crystal
103 pair with a fixed beam exit was used as a monochromator. The X-ray beam was aligned to
104 an intermediate focus, and then collimated by slits located at the distance of the
105 intermediate focus to about $100 \times 100 \mu\text{m}^2$ and subsequently focused with a Kirkpatrick-Baez
106 mirror pair to about $40 \times 30 \mu\text{m}^2$ at the sample position.

107 The μ -XAS spectra were measured either in transmission mode at W L_1 and L_3 edges or in
108 fluorescence mode at the V K , Cr K , and Fe K edges. The intensity of the primary beam was
109 measured by an ionization chamber. The second ionization chamber was used to measure
110 absorption of the beam in the sample and the third ionization chamber the absorption of
111 the beam in the standards. Fluorescence intensities were collected with a seven-element
112 Si(Li) solid state detector with the energy window set to the respective emission line. Data
113 were dead time-corrected, summed up for all seven channels and divided by the input
114 intensity, which was measured in an ionization chamber prior to the sample. The spectra
115 were collected in energy steps of 5 eV in the region from -150 to -50 eV relative to the
116 absorption edge, of 2 eV in the region from -50 eV to -20 eV, of 0.5 eV from -20 eV to $+20$
117 eV, and with a k step of 0.05 from $+20$ eV to $+400$ eV (about $k = 10$). The standards used
118 were metal foils of the metal measured (either V, Fe, Cr, or W). In addition, selected
119 reference compounds were also measured (e.g., siderite, hematite). The collected data were
120 processed by ATHENA and ARTEMIS (Ravel and Newville 2005).

121 Non-polarized Raman spectra were measured from polished sections with a LabRAM HR
122 (Horiba Jobin-Yvon) microspectrometer, Olympus BX41 microscope, and confocally coupled
123 Czerny-Turner type monochromator (focal length 800 mm). The Raman scattered light was
124 collected at 180° geometry through a 100×/0.80 objective lens and dispersed by a
125 diffraction grating with density 600 gr.mm⁻¹ onto a cooled CCD detector. The system
126 resolution was less than 6 cm⁻¹, and the wavenumber accuracy was ±1 cm⁻¹. The grating
127 turret accuracy was calibrated between zero-order line (180° reflection) and laser line at 0
128 cm⁻¹. Spectral accuracy was verified on 734 cm⁻¹ line of Teflon. A laser emission at $\lambda =$
129 532.09 nm (frequency-doubled Nd-YAG laser) was used for excitation. Laser power was
130 dimmed to 1.6 mW on sample surface. Spectra were acquired in the range of 70-4000 cm⁻¹,
131 exposition time was 300 s.

132 Slicing and polishing of lamellae for TEM analysis were carried out using a scanning
133 electron microscope (SEM) coupled with a gallium focused ion beam (FIB) source. The SEM-
134 FIB (Helios G4 UX, ThermoFisherScientific) equipped with a high-performance FIB source
135 (Phoenix) allows polishing of TEM lamella at very low acceleration voltage or beam current.
136 The lamellae obtained by FIB were characterized by low magnification transmission electron
137 microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and scanning
138 transmission electron microscopy (STEM) using high-angle annular dark field (HAADF)
139 detector. The TEM and STEM characterization was done with a double corrected JEOL JEM
140 ARM200cF (S)TEM microscope equipped with a cold field-emission gun operated at 200 kV.
141 For all STEM HAADF measurements, probe convergence angle of 22 mrad was used. HAADF
142 detector inner and outer semi-angles were 90 and 370 mrad, respectively. All data were
143 processed with 64-bit Digital Micrograph GMS 3.21 (Gatan).

144 **Results**

145 Elemental composition and zoning

146 In the studied mineralization, rutile is a common microscopic mineral that is found in quartz
147 or silicified and altered country rocks (Fig. 1a), in association with molybdenite (Fig. 1b) or
148 pyrite (Fig. 1c). Microscopic observations suggest that rutile was formed as an early mineral,
149 probably coeval with ferberite, magnetite, and ilmenite. These minerals were then replaced
150 by titanite and scheelite in a later Ca-metasomatic event. Magnetite is often cracked and
151 oxidized to hematite. Among the Ti minerals, only rutile contains high amount of W (Fig. 2a).
152 One spot analysis in ilmenite detected 1.1 wt.% WO_3 but its content is otherwise less than
153 0.3 wt.%. The WO_3 concentration in titanite does not exceed 0.15 wt.%.

154 Chemical composition of the rutile crystals is highly variable and reflects, to some extent,
155 also the nature of the host rocks. Striking variations are found also within a single crystal,
156 not only between crystals in different samples. No correlation was found between the bulk
157 W concentrations in the sampled drill-core sections and the W concentrations in the spot
158 analyses in the rutile crystals. Throughout the mineralized zone (down to the depth of 87
159 m), rutile crystals contain patches with high WO_3 concentrations. No sampling was done
160 outside or below the mineralized zone and it is not clear if such W-rich rutile could be used
161 as a pathfinder mineral to locate such deposits, as addressed by one of the reviewers. We
162 will attempt to answer this interesting question in a following study.

163 Some parts of the rutile crystals correspond chemically almost to pure TiO_2 . In many
164 cases, the second most abundant metal is tungsten, with concentrations of up to 17.7 wt.%
165 WO_3 (Table 1). All electron microprobe analyses are listed in Table S1. In samples where the
166 host rocks contain intercalations of metabasic or metaultrabasic rocks, the rutile crystals are

167 distinctly enriched in chromium (up to 7.5 wt.% Cr₂O_{3,tot}) and vanadium (up to 4.1 wt.%
168 V₂O_{3,tot}) (Table 1, Fig. 2b). Iron is also common, with up to 7.3 wt.% FeO_{tot}. The
169 concentrations of other elements is shown in a box-and-whisker diagram in Fig. 2d. The low
170 concentrations of Sn, Ta, and Nb agree with the general mineralogy of this W-Mo deposit
171 which is devoid of cassiterite or minerals of Nb-Ta.

172 The tungsten-rich parts of rutile crystals are also enriched in other metals (other than Ti)
173 and the fraction of tungsten does not exceed 0.5 (Fig. 2c). Another way to observe such
174 dependence are the high to moderate correlation factors between W and other metals (r^2_{W-Fe}
175 $= 0.80$, $r^2_{W-V} = 0.82$, $r^2_{W-Cr} = 0.51$). There is only weak correlation between the less
176 abundant elements in rutile (e.g., $r^2_{V-Cr} = 0.26$).

177 The elements are distributed in the rutile crystals inhomogeneously, in patches or
178 outermost growth zones. In the grain T (Fig. 3), the core is almost tungsten-free and the
179 overgrowth shows patches with variable, locally high content of W, Fe, Cr, and V. Many
180 smaller rutile grains have no such cores and are built only by patches with variable content
181 of metals (metals other than Ti).

182 For further investigation, two crystals were selected – crystal T (Fig. 3) and crystal 9 (Fig.
183 1a). Although they are heterogeneous, they contain elevated W in some patches and they
184 are large enough for the X-ray microbeam techniques.

185 X-ray absorption and Raman spectroscopy

186 Raman spectra of rutile zones with compositions near TiO₂ (Fig. 4, spectrum a) are
187 comparable to the spectra of synthetic, phase-pure rutile (Hofmeister et al. 1990). The
188 bands at 141, 440, and 615 cm⁻¹ correspond to the B_{1g}, E_g, and A_{1g} modes, respectively. The
189 broader band at 249 cm⁻¹ can be assigned to second-order Raman scattering. A weak

190 shoulder at 838 cm^{-1} could represent the B_{2g} mode. With increasing concentration of metals
191 other than Ti, the overall intensity of the bands diminishes and the band become broader.
192 The three distinct bands, visible also in almost pure rutile, shift slightly to 139, 437, and 625
193 cm^{-1} . Another strong band at 706 cm^{-1} appears and its asymmetry towards higher
194 wavenumber suggest that it may be composed of several peaks. At wavenumbers between
195 $3000\text{-}4000\text{ cm}^{-1}$, the spectra are completely featureless.

196 The X-ray absorption spectra at the different absorption edges were normalized and
197 inspected for similarities or dissimilarities. If similar, the spectra were merged and
198 compared to the standard spectra, either those measured in this work or those in the
199 spectra library (<http://cars.uchicago.edu/xaslib/search>). At each edge, spectra were aligned
200 so that the first inflection point of the calibration spectra of metal foils matched. The
201 positions of the edges were defined as the energy where the intensity is 50 % of the edge
202 maximum (Henderson et al. 2014).

203 The X-ray absorption near-edge structure (XANES) spectrum for tungsten (Fig. 5a,b) was
204 measured at both L_1 and L_3 edges. Absorption was stronger at the L_3 edge, resulting in a
205 much better signal-to-noise ratio. The white line at this edge shows splitting into two peaks,
206 used in the literature as evidence of octahedral coordination of W^{6+} (cf. Yamazoe et al.
207 2008). This is also confirmed by the absence of a pre-edge feature at the L_1 edge (Fig. 5a).

208 At the Fe K edge (Fig. 5c), the shape of the spectra differed between the two examined
209 crystals. In the crystal 9, the steep rise coincided essentially with the spectrum of magnetite,
210 suggesting a mixed valence of Fe. There is an additional feature just below the peak of the
211 white line which is not seen in any of the reference spectra. Only the reference spectrum of
212 FeO has such shoulder that precedes the white-line maximum. In the crystal T, the steep rise

213 roughly overlaps with that for the hematite reference; actually, it is even slightly shifted (1
214 eV) to higher energies, suggesting that Fe in this crystal is only in its trivalent state.

215 The spectrum at the vanadium *K* edge (Fig. 5d) shows only a weak pre-edge feature and
216 the steep rise of the edge is positioned between the reference spectra of V₂O₃ and VO₂.
217 Fitting of the spectra of the reference compound with known formal oxidation state (insert
218 in Fig. 5d) gave an average oxidation state of +3.8 for vanadium in our samples. For the
219 fitting, the spectra of V₂O₃, V₂O₅, VO, and VO₂ were used. The positions of 20 %, 50 %, or 80
220 % of the white-line maxima for these spectra define a trend that can be fitted very well ($r^2 =$
221 1) with a second-order polynomial. Metallic V, as expected, does not fit in this trend
222 because of the very different coordination of the V atoms in the oxidic references and in the
223 metal.

224 At the Cr *K* edge (Fig. 5e), the spectra for the two crystals were essentially identical. The
225 determination of the oxidation state is complicated by the shape of the spectra where the
226 evaluation at the different positions (20 %, 50 %, 80 % of the maximum height of the white
227 line) give significantly different results. Additionally, the spectra of the chromate (crocoite)
228 and dichromate (NH₄ dichromate) also show shift in the position of the edge, thus
229 introducing another uncertainty. It seems that the average oxidation state near 4. There is
230 also a very weak pre-edge feature, attesting to fully octahedral coordination of Cr in our
231 samples.

232 Comparison of the Cr, V, and Fe XANES spectra from the studied rutile crystals (Fig. 6)
233 shows that their shapes deviate, suggesting perhaps differences in the local structures of
234 these elements. In the spectra for Cr and V, there is an additional strong feature 6 eV above
235 the maximum of the white line (marked B in Fig. 6) and a weaker feature 16 eV above
236 (marked C in Fig. 6). The spectra of hematite-type compounds also possess the B feature but

237 lack the C feature. Interestingly, although the local environment is identical for all elements
238 (Ti, V, Cr, Fe) in these compounds, the Fe *K* spectrum has much weaker B feature. Among
239 the TiO₂ polymorphs, rutile has both B and C features pronounced whereas the C feature is
240 somewhat weaker in brookite. Hence, the Cr and V spectra of the studied rutile resemble
241 qualitatively the Ti spectrum of rutile, although they are shifted to somewhat lower
242 energies.

243 Shell-by-shell fitting was done for the extended X-ray absorption fine-structure (EXAFS)
244 data collected at the W *L*₃ edge. The starting model was generated by slicing a fragment of
245 the rutile structure and inserting a W atom at one of the Ti positions, central in the
246 fragment. The fragment was large enough so that none of the atoms considered for the
247 calculation of the scattering paths had dangling bonds. This initial model was able to fit the
248 data well and needed only minor adjustment to account for the W-O distance larger than the
249 Ti-O distance. The model also considered multiple scattering W-O-O-W paths. The final
250 model considered all O and Ti atoms up to a distance of 6 Å from the central absorber (Fig.
251 7a,b), but the number of variables was kept to 13, much smaller than the number of
252 independent data points (28.3, Table 2). No attempts were done to distinguish between the
253 neighboring Cr, V, Ti, or Fe, as these elements have similar scattering power.

254 There are slight differences between the results for the two crystals. In crystal 9, the
255 central W atom is coordinated by 6 O atoms with the W-O distance of 1.90 Å (Table 2). In
256 the crystal T, the first coordination sphere of the W atom is distorted, with three W-O
257 distances of 1.87 Å and another three at 1.91 Å. There are also small differences between
258 the distances refined for the longer W-O and W-Ti paths, reflecting perhaps the different
259 elemental compositions of the clusters that include the W atoms in the structure. Overall,

260 however, the model conforms very well to a local rutile-like environment for the tungsten
261 atoms in both examined crystals.

262 Transmission electron microscopy

263 The crystal T (Fig. 3) was used for the focused ion beam slicing and subsequent examination
264 in a transmission electron microscope. The position of the slice is shown in Fig. 3, cutting
265 through the exposed W-richest portions of the crystal. In the depth, the slice intercepted
266 also portions which are not as rich in tungsten as those visible in the BSE image.

267 The entire slice consisted of a single crystal of rutile, as documented by inspection of
268 many images, measurement of interplanar distances and indexing of electron diffraction
269 patterns (Fig. 8, S1). The interfaces between the W-rich and W-poor patches of the crystal
270 are diffuse but the orientation of the lattice in the two patches is coherent (Fig. 8, S1). There
271 were no signs of another phase in the form of inclusions or exsolutions in the W-rich
272 portions. The electron diffraction patterns of the W-poor and W-rich part of the rutile
273 crystals provided no indication of a superstructure formation or a departure from the
274 tetragonal symmetry of rutile.

275 Discussion

276 The flexibility of the rutile structure is documented in the natural samples of rutile and
277 the isostructural cassiterite. In rutile, the most common metal other than Ti is usually Fe but
278 other cations may be taken up as well. Clark and Williams-Jones (2004) listed a number of
279 analyses of natural rutile as an indicator of the presence of ore deposits. Tungstenic rutile
280 has been described from a number of sites in the world (Kwak 1983, Rice et al. 1998, Clark
281 and Williams-Jones 2004, Müller and Halls 2005, Novák et al. 2008, Mozola et al. 2017, Yang

282 et al. 2018). High W-Cr-V-Nb contents were reported also from metamorphic rutile
283 (Reznitsky et al. 2017). The formation conditions extend from those typical for granulite-
284 facies metamorphism (Reznitsky et al. 2017), pegmatite bodies (Mozola et al. 2017) down to
285 late low-temperature hydrothermal overprint (Rice et al. 1998). In some rocks, more than
286 90 % of their bulk W content can be stored in rutile (Meinhold 2010). In some cases, rutile in
287 the country rocks of ore deposits was found to be rich in Nb-Ta but low in W (van Gaans et
288 al. 1995). It was assumed that W was leached from an early W-bearing rutile, only to be
289 deposited later in quartz veins as wolframite. Cassiterite, a mineral with the rutile structure,
290 was also found to be enriched in tungsten and other elements (Wille et al. 2018, Moscatti
291 and Neymark 2020; Bennett et al. 2020). The proposed substitutions mechanisms in many
292 of these studies, although feasible from a point of view of crystal chemistry, are rarely
293 supported by data other than electron microprobe analyses.

294 Another possibility of incorporating elements of various charge into a rutile-like structure
295 is the formation of superstructures. The trirutile superstructure contains many members – a
296 natural one such as tripuhyite (FeSbO_4 , Berlepsch et al. 2003) and many more synthetic
297 tantalates, tellurates, bismuthates, etc. (e.g., Kumada et al. 1997, Matsubara et al. 2017,
298 Baral et al. 2019). Hence, the rutile structure is as flexible in accommodating various cations
299 as similar, simple structures based on *ccp* or *hcp* arrangement of the anions (spinel,
300 perovskites, sesquioxides). If a certain limit is exceeded, a new phase will exsolve and host
301 the cation(s) which do not fit into the original structure (e.g., Escudero et al. 2012).

302 The rutile crystals investigated here contained a significant amount of W, Cr, V, and Fe.
303 The TEM observations (Fig. 8) provided no evidence of long-range ordering and formation of
304 superstructures, even in the regions with high W concentration. The XAS data confirmed
305 that all cations are coordinated octahedrally (Fig. 5). For W, it was shown by shell-by-shell

306 XAS fitting (Fig. 7) and for all these cations by weak or no pre-edge features in the XANES
307 region. Even though the EXAFS analysis was carried out only at the W L_3 edge, there is no
308 reason to assume that the other cations are not incorporated in the rutile structure.
309 Another strong indication is the fraction of W, the only element with nominally higher
310 charge than +4, that was limited to 50 % among elements other than Ti in the W-rich parts
311 of the rutile crystals (Fig. 2c). This means that the structure seeks and finds local charge
312 compensation by creating clusters of W^{6+} and cations with oxidation state of less than +4.
313 Similar conclusions were reached for W-enriched cassiterite (Möller et al. 1988) where the
314 $W/(Fe+Mn)$ ratio was near 0.5, suggesting a $W^{6+} + 2Fe^{3+} \leftrightarrow 3Sn^{4+}$ substitution. The
315 determination of the oxidation state of Fe was supported in this case by bulk Mössbauer
316 spectroscopy.

317 The possibility that hydrogen atoms may be involved in local charge compensation,
318 perhaps in the combination with creation of vacancies (e.g., Rice et al. 1998), was refuted in
319 this work by Raman spectroscopy (Fig. 4). The existence of OH groups was confirmed by
320 infrared spectroscopy in rutile and cassiterite samples (Maldener et al. 2001, Losos and
321 Beran 2004) who proposed that the abundance of the OH groups may be a function of
322 water activity in a given hydrothermal system. Additional support for the presence of H in
323 rutile and cassiterite was provided by EPR studies (Dusausoy et al. 1988, Ruck et al. 1989)
324 and neutron scattering (Swope et al. 1995). Theoretically, the possibility of the hydrogen
325 doping in cassiterite has been tested and confirmed by Borges et al. (2015).

326 In a few of these studies, the substitution mechanisms for rutile were proposed. Rice et
327 al. (1998) considered a simple Fe-W substitution, with Fe either in the ferrous or ferric form.
328 Additionally, they invoked vacancy formation at the oxygen position. This supposition is
329 definitely not supported by our work where all cations were found to be coordinated

330 octahedrally. No oxygen vacancies were detected in this way, although we have to admit
331 that XAS is not sensitive to trace amounts of other coordination types or vacancies.
332 Reznitsky et al. (2017) considered much more complicated coupled substitutions in their W-
333 Cr-V-Nb-rich rutile. Such contemplations are based on the nominal charges of elements. This
334 study documents an additional complication and that is the variable oxidation state,
335 especially for V, Fe, but also Cr. Chromium under moderately reducing conditions, for
336 example, is not limited to its nominal Cr³⁺ oxidation state, in various phases including TiO₂
337 polymorphs (Kollbek et al. 2015, Suzuki et al. 2016). We also found that electron microprobe
338 analyses, usually used for the determination of the substitution mechanisms, do not possess
339 the necessary accuracy unless the substitution is very simple, for example limited only to
340 WFe₋₁.

341 There are numerous possibilities for charge balancing within the local clusters, for
342 example



346 and so on. We stress once again that these are examples and there may be many other
347 combinations. Because of the similar scattering power of the elements Fe, Cr, V, XAS data
348 alone cannot be used to distinguish if some combinations are preferred.

349 Some of the rutile and cassiterite crystals, described in the publications cited above,
350 could adopt the same simple substitution scheme as defined in this work. In other cases,
351 however, it seems that the OH group may play an important role. The proposition of Izoret
352 et al. (1985) that the substituting cations in the cassiterite structure occupy interstitial sites
353 would need to be confirmed on suitable samples by modern techniques. Given that the rutile-
354 type structures are densely packed, we view such mechanism skeptically. In some cases,

355 other substitution mechanisms must be sought. In the work of Bennett et al. (2020),
356 cassiterite crystals had W-rich sectors with no other substituting cations in abundance. The
357 possibility of the presence of W^{4+} should be explored or perhaps there are nano-inclusions of
358 separate tungstenic phases in these crystals.

359 **Implications**

360 The ore-forming potential (for Sn-W ores or LCT pegmatites) of an igneous complex has
361 been assigned primarily to enrichment of source lithologies by elements such as Sn, W, Li,
362 Rb, Cs, Nb, and Ta and the depletion of Ca, Sr, and Ba (e.g., Romer and Kroner 2016). Such
363 geochemical signatures could be also reached by extreme fractional crystallization but in
364 that case, much greater degree of melting would be expected. Our work implies that the
365 most efficient carriers of W in such enriched 'source lithologies' are titanium oxides. The
366 detrital Ti oxides in sediments are too refractory to react and take up elements such as W.
367 Rock-forming minerals (e.g., biotite, amphibole) can be weathered and degraded to a
368 plethora of low-temperature minerals, including Ti-oxide mixture named 'leucoxene'. It
369 could serve as a primary scavenger and carrier of W in sediments; the charge compensation
370 for W^{6+} in Ti oxides can be achieved by many different cations. The assertion of Romer and
371 Kroner (2016) that W can be carried by clay minerals is unlikely. Indeed, Cave et al. (2017)
372 showed that W enrichment was facilitated by prograde breakdown of rutile to titanite in
373 Otago schist, New Zealand.

374 Thus, rutile may be a very efficient vehicle for W in metamorphic and magmatic systems,
375 as long as the it is not converted to other minerals, e.g., titanite (Cave et al. 2017). Under
376 the conditions of high whole-rock Ca activity (Angiboust and Harlov 2017), the liberated
377 tungsten is deposited in scheelite. If this rutile carries also Sn, this element could be easily

378 incorporated into the newly formed titanite (e.g., Aleksandrov and Troneva 2007, Cempírek
379 et al. 2008, Ordosch et al. 2019), garnets (e.g., Dadák and Novák 1965, Mulholland 1984), or
380 other silicates. The ability of numerous metamorphic silicates to retain Sn but not W is an
381 efficient mechanism for decoupling of the two elements in high-temperature processes. On
382 the other hand, some skarn garnets were shown to retain both Sn and W, thus hindering
383 their decoupling (Xu et al. 2016).

384 Iron oxides in sediments could be another option of W retention and transport. Since
385 aqueous W forms an anion (WO_4^{2-}), it has a strong tendency to adsorb onto iron oxides. This
386 adsorption, however, is a subject of harsh competition, and phosphate is usually seen as the
387 strongest adsorbent, stronger than arsenate or other anions (e.g., Zeng et al. 2008). Under
388 specific, albeit imprecisely known conditions, W can be stored in the structures of hematite
389 and goethite in weathering environments (Tarassov et al. 2002, Kreißl et al. 2016). Even
390 elements considered to be highly immobile (e.g., Nb, Friis and Casey 2018), may be
391 efficiently transported by aqueous solutions in some low-temperature systems. The
392 mechanism proposed by Kreißl et al. (2016) involves vacancy formation and complex charge
393 compensation and can be, therefore, seen as a metastable arrangement. It is likely that such
394 W would be released and potentially lost upon recrystallization during diagenesis or
395 prograde metamorphism.

396 Hence, tungsten can be transported efficiently by rutile. Muscovite or biotite breakdown
397 (Romer and Kroner 2016) could be indeed responsible for release of elements such as Li, Cs,
398 Rb into the melts but the principal carrier of W in metasediments is probably rutile (cf. Cave
399 et al. 2017).

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407

408 **Table 1.** EMP analyses of the rutile crystal T from Ochtiná. Positions of the analytical spots are shown
 409 in Fig. 3 and labeled with the same numbers of analytical spots as in this table. All analyses are listed
 410 in supplementary information and displayed in Fig. 2. <DL = below detection limit

spot #	SnO ₂	Nb ₂ O ₅	WO ₃	Ta ₂ O ₅	Al ₂ O ₃	FeO	Cr ₂ O ₃	V ₂ O ₃	TiO ₂	Sc ₂ O ₃	MnO	Total
weight %												
5	0.25	0.07	17.68	<DL	0.08	3.09	3.28	3.62	74.42	0.06	0.03	102.63
6	0.33	0.10	16.86	<DL	0.12	3.27	2.50	3.95	74.27	0.08	0.08	101.58
7	0.27	0.09	17.73	<DL	0.13	3.17	2.98	3.85	74.10	0.05	0.09	102.50
8	0.02	0.23	0.05	<DL	<DL	0.21	0.03	0.39	100.36	<DL	<DL	101.29
9	0.22	0.07	14.40	<DL	0.11	2.41	3.10	3.72	76.63	0.07	0.03	100.78
10	0.42	0.09	10.57	0.05	0.06	1.51	2.90	2.71	82.11	0.02	<DL	100.45
11	0.24	0.10	6.15	0.02	0.03	0.64	2.70	1.12	90.14	0.03	0.05	101.24
12	0.28	0.10	2.52	<DL	0.03	0.60	0.76	0.88	96.22	0.02	0.04	101.47
13	0.31	0.06	9.60	<DL	0.08	1.31	2.67	2.31	85.41	0.05	<DL	101.79
14	0.24	0.15	6.45	<DL	0.03	0.63	3.28	0.92	88.65	0.02	<DL	100.36
15	0.26	0.07	15.23	<DL	0.10	2.58	3.12	3.42	76.30	0.03	0.02	101.14
atomic proportions normalized to 1 cation												
	Sn	Nb	W	Ta	Al	Fe	Cr	V	Ti	Sc	Mn	
5	0.003	0.001	0.212		0.001	0.036	0.034	0.037	0.675	0.001	0.000	
6	0.004	0.001	0.205		0.001	0.039	0.026	0.041	0.681	0.001	0.001	
7	0.003	0.001	0.213		0.001	0.037	0.031	0.040	0.672	0.001	0.001	
8	0.000	0.003	0.001			0.003	0.000	0.004	0.989			
9	0.003	0.001	0.178		0.001	0.029	0.033	0.039	0.715	0.001	0.000	
10	0.005	0.001	0.133	0.001	0.001	0.019	0.031	0.029	0.780	0.000		
11	0.003	0.001	0.078	0.000	0.000	0.008	0.030	0.012	0.866	0.000	0.001	
12	0.004	0.001	0.032		0.000	0.008	0.008	0.010	0.936	0.000	0.001	
13	0.004	0.001	0.120		0.001	0.016	0.029	0.025	0.805	0.001		
14	0.003	0.002	0.083		0.000	0.008	0.036	0.010	0.858	0.000		
15	0.003	0.001	0.187		0.001	0.031	0.033	0.036	0.708	0.000	0.000	

439 **Table 2.** Results of fitting of the W L₃ EXAFS data for the rutile crystal 9. The data and fits are
 440 also displayed in Fig. 7a,b. $\Delta E_0 = 6.4$, $N_{\text{var}} = 13$, $N_{\text{ind}} = 28.3$, $R = 0.044$, k range = 3.0-12.0 Å⁻¹,
 441 R range = 1-6 Å.

W-O			W-Ti			W-O-O-W		
<i>n</i>	<i>d</i> (Å)	1000 × σ^2	<i>n</i>	<i>d</i> (Å)	1000 × σ^2	<i>n</i>	<i>d</i> (Å)	1000 × σ^2
3	1.898(9)	4	1	3.043(2)	2	16	3.218	2*ss1
3	1.895(9)	4	1	3.043(5)	2	4	3.291	2*ss1
4	3.355(9)	2	4	3.560(9)	2	4	3.760	2*ss1
4	3.428(9)	2	4	3.653(5)	2	2	3.826	2*ss1
8	3.950(9)	2	4	4.53(2)	2			
2	4.45(2)	5	4	5.47(2)	5			
8	4.71(2)	5	4	5.61(2)	5			
4	4.55(2)	5	4	5.51(2)	5			
4	5.54(2)	5	4	5.64(2)	5			
4	5.44(2)	5	2	5.85(2)	5			
8	5.69(2)	5						
8	5.99(2)	5						

458 Figure captions

- 459 **Fig. 1.** Reflected-light images, showing the associations of rutile with other minerals in the
460 samples studied. a) Rutile (rt) crystal in altered and silicified metamorphic rock, made of
461 a fine-grained mixture of chlorite, epidote, and altered amphibole. This is the crystal 9,
462 used for XAS spectroscopy. b) Rutile in an aggregate of molybdenite (moly) crystals in
463 quartz. c) Rutile in pyrite (py) and quartz and sheet silicates.
- 464 **Fig. 2.** Concentration of selected oxides or elemental ratio in rutile and associated minerals
465 from Ochtiná. All data shown in a,b,c are spot electron microprobe analyses. White
466 symbols in c) are electron microprobe data from Yang et al. (2018). In c), not all elements
467 Fe, Al, Nb, Ta, V, Cr, Mg were analyzed in every spot. Those that were not analyzed in a
468 given spot are set to zero when constructing this figure. d) Box-and-whisker diagram
469 (constructed from spot EMP analyses) for oxide concentrations in rutile. The edges of the
470 boxes show the lower and upper quartile, the line within the box the median. The ranges
471 of the data are shown by the whiskers.
- 472 **Fig. 3.** Back-scattered electron (BSE) image and distribution of selected elements in the
473 rutile crystal T, used for Raman, XAS spectroscopy and TEM investigation. The positions
474 where the two Raman spectra (**Fig. 4**) were measured are shown by red crosses in the
475 BSE images. The orientation of the FIB slice, used for the TEM work, is indicated by the
476 blue rectangle. The position of EMP analytical spots are shown by circles (black or white;
477 color only chosen to enhance contrast) and the numbers correspond to analyses
478 presented in **Table 1**.
- 479 **Fig. 4.** Raman spectra of W-poor (a) and W-rich (b) parts of the rutile crystal T. The letters **a**
480 and **b** refer also to the positions where the spectra were measured, shown in **Fig. 3**. The
481 spectrum labeled as “reference” is a Raman spectrum of pure synthetic rutile (Lafuente
482 et al. 2015).
- 483 **Fig. 5.** XANES spectra from the rutile crystals T and 9, at different absorption edges,
484 compared to spectra of selected reference compounds. The spectra are labeled T or 9 for
485 the two crystals or T,9 if the spectra for the two crystals were very similar. The inset in d)
486 shows the results of fitting of the edge position (50 % of the maximum height of the
487 white line). Red circles represent positions of the reference compounds, the blue star the
488 position determined from the spectra for the rutile crystals studied. From this position,
489 the average oxidation state of V has been calculated.
- 490 **Fig. 6.** Comparison of XANES spectra of reference compounds and rutile from Ochtiná at
491 different absorption edge. The spectra were shifted so that the positions of the
492 calibration spectra (native metals) overlap.
- 493 **Fig. 7.** The EXAFS and Fourier-transform EXAFS spectra (at the W L_3 edge) of the W-enriched
494 portions of the rutile crystals. Circles and thin lines represent the measured and
495 processed data, the thick colored lines represent the fits. For further details, see text.
- 496 **Fig. 8.** a) W-rutile crystal depicting W-rich and W-poor domains oriented along $[10\bar{1}]$
497 direction. The selected area diffraction patterns (right) show the diffraction spots from
498 the W-poor (white) and W-rich (yellow) parts of the rutile crystal. b) Interface between
499 W-rich/W-poor regions is coherent which is indicated by straight and continuous lattice
500 fringes. c) Detailed atomic resolution HAADF STEM image of the W-rich domain. Bright
501 spots represent Ti columns in rutile crystal structure. The brightest spots in this image
502 indicate Ti+W columns.
- 503

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