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1 **Thermodynamic determination of condensation behavior for the** 2 **precursory elements of radioxenon following an underground** 3 **nuclear explosion**

4 Bernard Bourdon¹, Eric Pili²

5 ¹Laboratoire de Géologie de Lyon (LGL-TPE), ENS Lyon, CNRS and Université Claude Bernard de Lyon,
6 46 allée d'Italie, 69364 Lyon Cedex 7, France.

7
8 ²CEA, DAM, DIF, F-91297 Arpajon, France.

9
10 **Keywords:** underground nuclear explosion, vaporization, condensation, indium, tin,
11 antimony, tellurium, iodine, xenon

12 13 **Abstract:**

14 The measurement of radioactive xenon isotopes (radioxenon) in the atmosphere is a tool used
15 to detect underground nuclear explosions, provided that some radioxenon escaped
16 containment and that fractionation leading to the alteration of the relative proportions of
17 these isotopes, is accounted for. After the explosion, volatilization followed by melting of the
18 surrounding rocks produces a magma where the more refractory radioactive species get
19 dissolved while the more volatile ones contribute to the gas phase that might escape. Indium,
20 tin, antimony, tellurium and iodine are the main fission products involved in the decay chains
21 leading to radioxenon. In this study, condensation as a function of temperature for these
22 precursors of radioxenon were determined using thermodynamic calculations for systems
23 with complex chemical composition corresponding to major environments of known
24 underground nuclear explosions and for a range of pressure values representative of the
25 cavity evolution. Our results illustrate a large difference between the relevant condensation
26 temperatures for the radioxenon precursors and the tabulated boiling temperatures of the
27 pure compounds often used as indicators of their volatility. For some precursory elements
28 such as tin, the often-considered Heaviside function represents an oversimplification of the
29 concept of condensation temperature, as condensation occurs over a temperature range as
30 large as 2000 K. This results from the speciation of the elements in the gas phase mainly driven
31 by the formation of oxides. Condensation also strongly depends on pressure while it
32 moderately depends on the bulk chemical composition of the system. This study shows the

33 importance and complexity of the condensation process following underground nuclear
34 explosions. It also shows how thermodynamic computations allow the prediction of the
35 quantity and the relative proportions of radioactive xenon isotopes in the gas phase in the
36 presence of magma, before their potential emission to the atmosphere. Better detection,
37 discrimination and understanding of underground nuclear explosions should arise by taking
38 into account the fractionation resulting from the condensation of the radionuclides producing
39 radioxenon in nuclear cavities.

40

41

42 **1. Introduction**

43 The atmospheric detection of four radioactive isotopes (131m , 133m , 133 and 135 where m
44 is for metastable) of xenon (Xe), altogether referred as radioxenon, possibly released at the
45 ground surface following an underground nuclear explosion is a means for the verification of
46 the Comprehensive nuclear Test Ban Treaty – CTBT – (UNODA, 1995; Carrigan et al., 1996;
47 Hourdin and Issartel, 2000). Owing to many complex phenomena that occur after the
48 explosion, it is difficult to relate the activity and relative proportions of the xenon isotopes
49 detected in the atmosphere with the radioxenon inventory initially present in the nuclear
50 cavity at depth. However, this is important to fully characterize the event. This difficulty
51 pertains to the complexity of decay chains following fission together with a rapid thermal
52 evolution and subsequent multiphase transport in geological media following the explosion
53 (e.g., Sun et al., 2014, Sun and Carrigan, 2016; Pazdaniakou et al., 2022) as well as the existence
54 of an atmospheric background radioxenon signal not derived from underground nuclear
55 explosions (Achim et al., 2016). One overlooked process that controls the availability of
56 radioxenon is the partitioning of its precursory elements between the melt and gas phases in
57 the nuclear cavity immediately after the explosion (Carrigan et al., 2020, Sun et al., 2021,
58 2022).

59 An underground nuclear explosion vaporizes the materials surrounding the detonation point
60 and further melts the adjacent rocks (Taylor 1973). Upon cooling, condensation of the
61 vaporized matter and melting of the cavity walls and debris leads to the production of a liquid
62 whose composition depends on the surrounding rocks, while the material added by the
63 nuclear device is comparatively small. As a result of nuclear fission, radioxenon is produced by
64 three independent decay chains (e.g., Plompen et al., 2020). In the 131 , 133 and 135 decay

65 chains (Figure 1), the main precursory elements for radioxenon are, successively, indium (In),
66 tin (Sn), antimony (Sb), tellurium (Te), iodine (I), which are all more refractory elements than
67 xenon (Xe). Therefore, depending on the cooling history of the nuclear cavity together with
68 the short-lived existence of the nuclides controlled by the decay chains, the precursory
69 elements may condense into the magma or on the colder surfaces of rocks (cavity walls or
70 chimney rubbles) before radioxenon may have escaped the nuclear cavity and started
71 percolation through the fractured geological media towards the atmosphere. If condensation
72 is sufficiently rapid compared to decay, the production of the various radioxenon isotopes in
73 the vapor phase of a nuclear cavity can be altered.

74 Thus, in order to make more accurate predictions about the composition of the Xe isotopes
75 possibly emitted to the atmosphere, it is necessary to know whether the precursory elements
76 will condense before radioxenon escapes the system. As such, the condensation temperatures
77 and vapor pressures of the elements give quantitative information on their existence in the
78 gas phase. In this study, we have determined the equilibrium conditions of the vapor-magma
79 system from which we deduced condensation temperatures and vapor pressures for the
80 chemical composition of silicate liquids produced by melting of basaltic or granodioritic rocks
81 after an underground nuclear explosion.

82

83 **2. Phenomenology of underground nuclear explosion and how it relates to our calculations**

84 Following a nuclear explosion, the energy is released within a timescale of microseconds and
85 propagates as a shock wave from the detonation point. In the region where enough shock
86 energy is deposited, about 70 tons (per kiloton (kT) of explosive energy) of material reaches
87 temperatures large enough to complete vaporization (Butkovich 1974a). Beyond this zone of
88 full vaporization, the deposited energy is sufficient to fully melt in the order of 1000 tons of
89 material (per kT of explosive energy), depending on the initial density of the rock (Butkovich
90 1974b). The vapor that is produced by the explosion expands and forms a cavity containing
91 both melt and vapor. The volume of the cavity is controlled by the depth of the explosion, the
92 energy released and the local rock nature, the density and the water content (Boardman et
93 al., 1964; Higgins and Butkovich, 1967; Higgins, 1970; Butkovich, 1974b). In our study, we have
94 focused on the initial system consisting of vapor and magma evolving with decreasing
95 pressure and temperature as the initial energy is dissipated in the geological medium. This
96 corresponds to an early stage depicted in Figure 7 of Schwartz et al. (1984) where the magma

97 exists together with a vapor phase in a spherical cavity (from ca. 500 msec) until the collapse
98 of the cavity roof into the magma puddle (a few seconds to a few hours later). This potentially
99 gives enough time for thermal and chemical equilibrium to take place between the magma
100 and the gas phases, relative to the timescales of the radioxenon decay chains considered here.
101 The system cools relatively rapidly and ultimately forms magmatic glass commonly analyzed
102 for its radioactive content. Most of the budget of refractory fission products is observed to be
103 contained in the magma (Borg 1975; Smith et al. 1996; 2003) rather than with the rubble that
104 piles up at a distance from the magma found at the bottom of the cavity. This is a strong
105 indication that the refractory elements that must have been initially vaporized upon the
106 explosion were mostly condensed in the magma, rather than being dispersed in the
107 surrounding geological medium. In contrast, there is evidence for a significant budget of more
108 volatile elements that could have been partly transported to some extent by a vapor phase in
109 the rubble pile, notably Sb (Smith et al. 1996; 2003) even if most of it is also contained in the
110 magma. Thus, it seems reasonable to assume that at least in the beginning, there is a thermal
111 and chemical equilibrium between the vapor phase and the magma as assumed in what
112 follows.

113

114 **3. Volatility of the elements and condensation temperatures**

115 Chemical elements are considered as volatile if they preferentially partition in the vapor phase
116 relative to condensed phases. One measure of this volatility is the condensation temperature.
117 However, the condensation temperature of an element is not a fixed thermodynamic quantity
118 since it depends directly on the ambient pressure. For a pure substance, in the case of a liquid-
119 vapor equilibrium, the condensation temperature is only defined at a given pressure and
120 corresponds to a point of the liquid-vapor curve in a P-T phase diagram. In this case, the
121 saturation vapor pressure at equilibrium is defined by the Clausius-Clapeyron law, which is
122 expressed for a vapor-liquid phase change. In the case of multi-component systems, such as
123 the one studied here, at a given pressure, there is a range of temperatures for which the
124 element considered will coexist in vapor phase and in liquid phase. The condensation curve is
125 the curve representing the condensed fraction of the element as a function of temperature at
126 a given pressure. In this context, it is common to define the condensation temperature as the
127 temperature corresponding to an equal partitioning (50%, expressed in number of moles)
128 between the condensed phase and the vapor phase.

129 Cosmochemists have defined condensation temperatures for a system with the chemical
 130 composition of the Sun at a pressure of 10^{-4} atm for all the elements of the periodic table
 131 (Lodders, 2003; Wood et al. 2019), this pressure corresponding roughly to that of the solar
 132 nebula in the vicinity of the Earth. Although these conditions do not correspond at all to that
 133 of nuclear explosions, it is informative to consider the condensation temperatures of the
 134 elements under these conditions (see Table 1). For pure substances, the boiling temperature
 135 is equal to the condensation temperature. For mixtures, the boiling temperature is
 136 composition-dependent and boiling will take place over a range of temperatures. The large
 137 difference between the condensation temperature and the boiling temperatures of the
 138 elements (Table 1) given at 1 atm comes largely from the pressure which is 10^{-4} atm. Another
 139 important parameter as will be discussed in detail is the bulk chemical composition of the
 140 studied system and the elemental speciation. By definition, the solubility of a volatile element
 141 in a silicate melt corresponds to the equilibrium concentration of this element in the melt at
 142 a given pressure. The condensation of an element in the silicate melt thus reflects its
 143 increasing solubility as the temperature is lowered, at a given pressure.

144

145 **Table 1 Condensation temperatures determined for cosmochemistry and boiling**
 146 **temperatures**

Element	Condensation temperature (K, at 10^{-4} atm)		Boiling temperature (K, at 1 atm) Lide (1990) and reference therein
	Lodders (2003)	Wood et al. (2019)	
In	492	536	2350
Sn	604	704	2876
Sb	890	979	1860
Te	665	709	1261
I	535	390	457

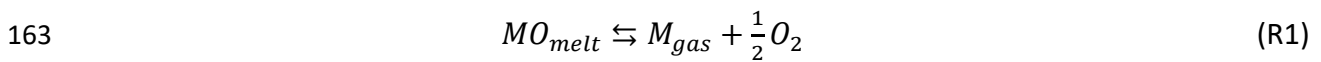
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148

149 **4. Oxygen fugacity, redox reactions and speciation**

150 Depending on the condensation reaction describing the equilibrium between the vapor and
 151 liquid phase, the effect of oxygen fugacity can play a key role on volatility. This was for example
 152 demonstrated in the study of Ebel and Grossman (2000) who simulated conditions where the
 153 mass fraction of solid (mostly oxides) increased relative to H_2 -dominant gas, which was

154 equivalent to increasing the oxygen fugacity. One observes that the condensation
155 temperatures of elements are highly dependent on this O_2 fugacity but this earlier work did
156 not include the trace elements (In, Sn, Sb, Te and I) that are the focus of the present study.
157 The experimental studies of Norris et al. (2017) and Sossi et al. (2019) have further illustrated
158 the dependence of oxygen fugacity for trace elements but could not determine the
159 corresponding condensation temperatures and vapor pressures for these elements due to
160 non-equilibrium conditions of their experiments. For most trace elements dissolved in an
161 oxide melt, the condensation temperature increases with oxygen fugacity (f_{O_2}). This can be
162 understood if one writes the vaporization reaction of a metallic oxide (MO_{melt}), as:



164 where M_{gas} is the vaporized metal species. If f_{O_2} increases, the reaction is favored towards
165 the condensed phase (i.e. MO_{melt}), which is equivalent to increasing the condensation
166 temperature. Thus, one needs to assess the redox state of the system and the speciation of
167 the considered elements in the melt and in the vapor, to determine their volatility as a
168 function of oxygen fugacity. These features as well as the dependence on the bulk composition
169 of the system will be presented in what follows.

170

171 **5. Thermodynamical approach**

172 *4.1. Initial conditions of the system and setup of the thermodynamic calculations*

173 The trace elements (In, Sn, Sb, Te and I) which are the focus of this study are generated as
174 fission products from the nuclear explosive and they initially partition in the vapor phase
175 formed from the volatilization of the surrounding rocks.

176 The studies of Brode (1964), Egorov et al. (1979) and Taylor (1973) were used to set the post-
177 explosion pressure and temperature conditions. The temperature and pressure conditions are
178 in a transient regime with variable time constants which depend on the energy initially
179 released during the explosion and later dissipated in the geological medium. The range in
180 pressure (orders of magnitude of hundreds of bar to 1 bar, considered from the moment the
181 chimney is formed) and temperature was chosen to cover the typical range reported in the
182 literature on these topics (e.g. Chapin 1970; Butkovich 1974a). Model curves depending on
183 the initial energy give the joint variation of T and P as a function of time (e.g., Egorov et al.
184 1979). These curves were used to establish the domains that needed to be explored from a

185 thermodynamic viewpoint. In this context, the pressure range used in this study was 1-100
186 bars (Taylor 1973; Egorov et al. 1979) and the temperature ranged between 500 and 4500 K.
187 An additional feature that one should bear in mind is that the volatility of elements will not
188 only depend on the thermodynamics but also on the kinetics, both of evaporation and
189 condensation, and we assumed for the sake of simplicity that chemical equilibrium was
190 reached. Some of these aspects are discussed below in section 8.1. By lowering the
191 temperature at a given pressure, the elements are progressively condensed in the liquid phase
192 starting with the most refractory to the most volatile.

193 As the relevant thermodynamic data were not available for temperatures greater than 2500
194 K, the thermodynamic parameters were extrapolated assuming that the parameterization
195 obtained in Table 4 is valid for the 500-4500 K range of temperature.

196 In order to test the potential effect of the bulk chemical composition of the system on
197 volatility, the condensation curves were calculated for two bulk silicate compositions reported
198 in Table 2, a granodiorite and a basalt. These chemical compositions are of interest because
199 they correspond to two extreme compositions typical of terrestrial rocks likely to be observed
200 at underground nuclear test sites. Granodiorites and basalts both occur at the Nevada
201 National Security Site (Sinnock 1982) or the Cannikin Site, Alaska (Lee and Gard 1971). Basalts
202 occur in most oceanic islands, particularly in atolls, such as the former French nuclear test sites
203 at Mururoa and Fangataufa (IAEA, 1998b). Granodiorite is also a close approximation of the
204 chemical composition of rocks from the Semipalatinsk (formerly USSR, now Kazakhstan)
205 nuclear test site (IAEA, 1998a) and of the North Korean nuclear test site at Punggye-ri
206 (Coblentz and Pabian, 2015). The composition of the granodiorite considered is a typical
207 composition taken from the GERM database (earthref.org/GERM). The composition of the
208 Mururoa basalt is taken from Dupuy et al. (1994). The In, Sn, Sb, Te and I contents are fixed
209 arbitrarily at 10^{-6} mol/100 g (*i.e.* in the range 0.11-0.13 ppm) such that they can be considered
210 as trace elements. This content is 1 to 2 orders of magnitude larger than the nuclear fission
211 contribution to each of these elements, considering conservatively 10^{-2} mol of each isotope
212 for a 1 kT explosion and 400 kg of melt (Sun et al., 2014; Carrigan et al., 2020). Hence, the
213 elemental concentrations considered here also account for the natural contents of rocks in In,
214 Sn, Sb, Te and I. The exact values selected here have no influence on the calculated
215 condensation temperatures, as long as the elements are at the trace level.

216

217 **Table 2: Chemical compositions of silicate rocks representing the bulk composition of the**
 218 **system.**

	Granodiorite ¹	Basalt ²
Oxides	wt %	wt %
SiO ₂	57.41	46.15
Al ₂ O ₃	16.7	16.53
TiO ₂	1.52	3.75
Fe ₂ O ₃	8.58	11.55
MnO	0.16	0.11
MgO	3.14	4.27
CaO	4.86	9.68
Na ₂ O	3.8	3.71
K ₂ O	3.04	1.41
P ₂ O ₅	0.29	0.45
H ₂ O	1.0	1.96

¹From GERM database, ²from Dupuyet al. (1994).

219 *4.2. Thermodynamic database and calculations*

220 The chemical equilibrium at various temperatures and pressures was calculated using the
 221 FactSage™ software (Bale et al. 2016), which includes thermodynamic databases for major
 222 elements as well as for many trace elements. The FToxid (oxide solutions) and FTpure (pure
 223 compounds) databases were used in this study. The Ftoxid database includes specific
 224 thermodynamic models for solutions of molten oxides (SLAG-A and SLAG-F). It is possible to
 225 manually add thermodynamic data, such as activity coefficients that are not part of the
 226 database, especially for dealing with trace element levels. We used this feature to include the
 227 trace elements In, Sn, Sb and Te. For the case of iodine, we used a specific molten oxide
 228 solution that includes I in the FactSage™ database (SLAG-F) which is distinct from the more
 229 complete oxide model used for the other elements (SLAG-A).

230 The FactSage™ software calculates thermodynamic equilibrium using minimization of the
 231 Gibbs energy of the total system. The total Gibbs energy of the system can be written as:

232
$$G_{tot} = \sum_j \sum_i \mu_i^j n_i^j \quad (1)$$

233 Where i represents a given constituent in a phase j and μ_i is the chemical potential of
 234 constituent i in phase j , n_i is the number of moles of constituent i . This equation can be further
 235 expanded to show the importance of activities and fugacities:

$$236 \quad G_{tot} = \sum_j \left(\sum_k (\mu_{k_0}^j + RT \ln f_k) n_k^j + \sum_l (\mu_{l_0}^j + RT \ln a_l) n_l^j \right) \quad (2)$$

237 where index k and i are for the vapor phase and condensed phases, respectively, and f_k and a_i
 238 are the fugacity and activity of component k and i respectively, in phase j . This approach
 239 requires a knowledge of all the thermodynamic properties of all the species contained in the
 240 vapor (i.e. their fugacities) and of the mixing properties of the liquid phase and of the solid
 241 phases that form solid solutions. Using the activities of all constituents, it is possible to
 242 calculate the partial Gibbs energy of each constituents (i.e. their chemical potential) and then
 243 optimize the phase proportions to minimize the total Gibbs energy of the system. These
 244 calculations assume that the whole system (with a bulk composition specified in Table 2 for
 245 the vapor+magma phases considered together) reaches chemical equilibrium at constant
 246 temperature and pressure, which is an important assumption whose validity is discussed in
 247 Section 8.2.

248 For a given T and P , the composition and abundance of each stable phase is calculated. The
 249 calculation also yields the speciation in the vapor phase. Our calculations were done at fixed
 250 pressures of 1, 10, 50 and 100 bars for temperatures ranging between 4500 and 500 K with
 251 temperature steps of 100 K.

252 The volatility of elements depends on their activity in the solid or liquid phase. For the
 253 vaporization reaction (R1), the equilibrium constant can be written as:

$$254 \quad K_{P,T} = \frac{f_M f_{O_2}^{1/2}}{a_{MO}} = \frac{f_M f_{O_2}^{1/2}}{\gamma_{MO} X_{MO}} \quad (3)$$

255 where f_i represents the fugacity of component i and a_{MO} is the activity of MO in the silicate
 256 melt, γ_{MO} its activity coefficient and X_{MO} its molar fraction. This equation shows that the
 257 volatility depends directly on the oxygen fugacity, a parameter controlled by the major
 258 element composition, rather than the trace element itself. While the vapor pressure will
 259 depend on the concentration of M in the source material, the calculated condensation
 260 temperature will be independent of this parameter because it is calculated by the ratio of
 261 molar abundances (see caption of Figure 3). This equation also shows that volatility expressed
 262 by the fugacity of vapor species $M(g)$ depends on the activity coefficient in the oxide solutions.

263 This parameter depends itself on the chemical composition of the system and on the
264 interaction parameters of element M with other constituents. We calculated volatility of In,
265 Sn, Sb, Te and I using literature data for the activity coefficients as reported in Table 3 following
266 the methodology described in the next section.

267

268 **6. Determination of activity coefficients**

269 The activity coefficients of In, Sn, Sb and Te have been measured experimentally for silicate
270 melts of various compositions but these data are not included in the FactSage™ databases. In
271 contrast, the FactSage™ SLAG-F database already includes activity coefficients for iodine in
272 silicate melts in dilute concentrations.

273

274 *6.1. Existing activity coefficients for iodine, indium, antimony and tellurium*

275 For iodine, it has been shown that the most of it is in the form of I^- (McKeown et al. Muller et
276 al. 2014; Cicconi et al 2020) and that iodide is often associated with alkalis (Na and K
277 essentially) or with calcium, which is consistent with the components present in the SLAG-F
278 solution of FactSage™. Previous experimental studies (Musselwhite et al. 2000; Cicconi et al.
279 2019; Riley et al. 2014; Jolivet et al. 2020) focusing on iodine solubility have not determined
280 directly the iodine activity in silicate melts and this would deserve dedicated experimental
281 studies in the future.

282 For indium, experimental determinations of activity coefficients reported in the study of
283 Norris (2016) give a mean value of 0.030 with a range from 0.0025 to 0.12 at a temperature
284 of 1923 K. For Sb, there are several determinations of the activity coefficient of $SbO_{1.5}$ in oxide
285 mixtures, including those given in Norris (2016). Mendoza et al. (2001) have determined the
286 activity coefficient for $SbO_{1.5}$ in CaO-FeO-SiO₂ mixtures as a function of the CaO content in
287 oxide melts and show variations of this parameter between 1.8 and 3.9 at 1573 K. These values
288 are rather close to the range in activity coefficients given in Norris (2016) at 1923 K (0.11-8.9,
289 mean=2.3). Thus, we have used values from the experiments of Norris (2016) and the results
290 are given in Table 4. A Raoult activity coefficient of $SbO_{1.5}$ equal to 1.14 at 1923 K was reported
291 by Tan et al. (2001). However, a Raoult activity coefficient corresponds to that of a solvent and
292 is equal to 1 for a molar fraction of $SbO_{1.5}$ equal to 1. This is not the same reference state as
293 that used for trace element where Sb is expected to be at infinite dilution (Henry activity
294 coefficient).

295 Johnston et al. (2010) reported values of the activity coefficients of Te in silicate melts (SiO₂-
 296 CaO-FeO) and showed a weak dependence on temperature and on CaO contents.

297

298 6.2. The case of tin: SnO versus SnO₂

299 Shuva et al. (2016) compiled the activity coefficients of SnO-SnO₂ in silicate mixtures, with
 300 values ranging between 0.8 and 6 (Rankin et al. 1986, Takeda et al. 1990; Nagamori and
 301 Mackey 1978). However, these values are relevant for SnO rather than for SnO₂ as these data
 302 were obtained at low oxygen fugacities, where SnO is the only stable species in the silicate
 303 melt. By comparison, the values of the activity coefficient for SnO₂ given in Norris (2016) for
 304 experiments in graphite capsules were orders of magnitude smaller (3×10⁻³ to 9×10⁻⁵). The
 305 same parameter was also estimated by Gortais et al. (1994) at a temperature of 1500 K but
 306 the oxygen fugacity was not given, yielding γ_{SnO_2} values between 0.2 and 2.5.

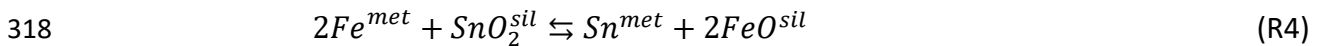
307 As this parameter can greatly affect the volatility of this element, in what follows, we first
 308 checked that the oxygen fugacity in the conditions of an underground nuclear explosion leads
 309 to the SnO₂ species, not SnO, to be dominant in the silicate melts. It is possible to extract the
 310 SnO₂ activity coefficients from reported experiments that were initially designed to determine
 311 the metal-silicate partition coefficient for Sn (Wood et al., 2013). These metal-silicate
 312 experiments involve the following exchange reaction for tin:

313



315

316 Combining with the reverse reaction for iron that represents the major element in the
 317 considered experiments, the reaction can be rewritten:



319 Its equilibrium constant can be expressed as:

$$320 \quad K = \frac{a_{\text{Sn}}^{\text{met}} a_{\text{FeO}}^{\text{sil}^2}}{a_{\text{SnO}_2}^{\text{sil}} a_{\text{Fe}}^{\text{met}^2}} = \frac{X_{\text{Sn}}^{\text{met}} X_{\text{FeO}}^{\text{sil}^2}}{X_{\text{SnO}_2}^{\text{met}} X_{\text{Fe}}^{\text{met}^2}} \cdot \frac{\gamma_{\text{Sn}}^{\text{met}} \gamma_{\text{FeO}}^{\text{sil}^2}}{\gamma_{\text{SnO}_2}^{\text{sil}} \gamma_{\text{Fe}}^{\text{met}^2}} \quad (4)$$

321 One can see that the equilibrium constant is a function of the parameter we are interested in
 322 (i.e. $\gamma_{\text{SnO}_2}^{\text{sil}}$). Thus, provided all the other parameters are known, one can express the activity
 323 coefficient of SnO₂ in the silicate melt as a function of the equilibrium constant K and the
 324 other parameters. First, this equilibrium constant can be calculated at the temperature of

325 interest using the free enthalpies of formation of the pure compounds Fe, FeO, SnO₂ and Sn
 326 reported in thermodynamic tables (Barin 1995). The free enthalpies of formation of each
 327 reagent and product are used to calculate the free enthalpy of the reaction R4:

$$328 \quad \Delta^R G = G_f^{Sn} + 2G_f^{FeO} - G_f^{SnO} - 2G_f^{Fe} \quad (5)$$

329 This equation is then converted to an equation giving the equilibrium constant of reaction R4:

$$330 \quad \text{Ln}K = \frac{-\Delta^R G}{RT} = 2\text{Ln}K_f^{FeO} + \text{Ln}K_f^{Sn} - (2\text{Ln}K_f^{Fe} - \text{Ln}K_f^{SnO_2}) \quad (6)$$

331 The formation constants of SnO₂ and FeO can then be parameterized as a function of 1/T using
 332 the data of Barin (1995), with the formation constant of pure Sn and Fe being equal to zero,
 333 by definition. One obtains for SnO₂ (valid between 1300 and 1800 K):

$$334 \quad \text{Ln} K_f^{SnO_2} = \frac{68377}{T} - 23.795 \quad (7)$$

335 and for FeO (equation valid between 1650 and 2500 K):

$$336 \quad \text{Ln} K_f^{FeO} = \frac{31217}{T} - 6.6503 \quad (8)$$

337 Based on these equations, one can extract the activity coefficient of SnO₂ in the silicate melt:

$$338 \quad \text{Ln} \gamma_{SnO_2}^{sil} = \text{Ln} \frac{X_{Sn}^{met} X_{FeO}^{sil}}{X_{SnO_2}^{met} X_{Fe}^{met}} \cdot \frac{\gamma_{Sn}^{met} \gamma_{FeO}^{sil}}{\gamma_{Fe}^{met}} - 2\text{Ln}K_f^{FeO} + \text{Ln}K_f^{Sn} - (2\text{Ln}K_f^{Fe} - \text{Ln}K_f^{SnO_2}) \quad (9)$$

339 The parameters X_{Sn}^{met} , X_{FeO}^{sil} , $X_{SnO_2}^{met}$, X_{Fe}^{met} can be determined for each bulk composition of
 340 the silicate melt in the metal-silicate experiments (as given in Righter et al. (2017) in the case
 341 of Sn) while the activity coefficients of FeO in the silicate melt are known from the literature
 342 (e.g., Wood and Wade 2013). The activity coefficient of metallic Sn in molten iron alloys can
 343 be calculated using the interaction parameters between the constituents of alloys as
 344 described in Ma (2001). The values of the interaction parameters have been recently compiled
 345 by Righter et al. (2017) and are also given in a compilation by the Japan Society for the
 346 Promotion of Science (1988). Since all the parameters of equation (8) can be calculated
 347 independently for the chemical composition of each reported metal-silicate experiment, it is
 348 then possible to calculate individual values of the activity coefficient of SnO₂ in the silicate
 349 melts. Thus, based on equation (8), one can determine from the above equations the values
 350 of $\gamma_{SnO_2}^{sil}$ although this parameter has never been directly determined experimentally.

351 By using this methodology, we have calculated the activity coefficients for two series of
 352 experiments, one with a graphite capsule and one with an MgO capsule (Righter et al. 2017).
 353 The activity coefficients obtained in both cases differ by at least one order of magnitude.

354 However, one should note that the experiments involving graphite (implying a large
 355 concentration of C in the metal) yield γ_{SnO_2} activity coefficients ranging between 10^{-2} and 10^{-4}
 356 which are comparable to those obtained by Norris (2016) with experiments involving also
 357 graphite. However, these experiments do not correspond to the situation found in
 358 underground nuclear explosions where the C level of the environment is rather low for the
 359 rock compositions studied here. We contend that an uncertainty on the interaction coefficient
 360 of C with Fe or Sn could produce differences in the γ_{SnO_2} values. The experiments of Righter et
 361 al. (2017) with an MgO container yield values that are closer to those of Gortais et al. (1994)
 362 and we have used these values to calculate the volatility of Sn (see below). Based on these
 363 values of the activity coefficient for SnO_2 , we obtained a regression line as a function of
 364 temperature (Figure 2). For a given chemical composition, temperature is the most important
 365 source of variation of the Sn activity coefficient.

366

367 *6.3. Parameterization of activity coefficients: dependence on temperature and on the*
 368 *chemical composition of the system*

369 We were able to obtain a set of activity coefficients, based on the above compilation of
 370 literature data for In, Sb and Te, and on the FactSage™ database for iodine, as well as on the
 371 calculation of Sn activity coefficient using the method described in Section 6.2. Some typical
 372 values are given in Table 3. One could note that these activity coefficients largely deviate from
 373 1. Given their temperature dependence, it is important to use a parameterization rather than
 374 a constant value, whenever possible, as detailed in what follows.

375 In order to express their variations as a function of temperature the following equation was
 376 used:

377
$$\ln(\gamma_i) = \frac{A}{T} + B \quad (10)$$

378 where A and B are constants that are determined experimentally.

379

380

381 **Table 3 Speciation and source of activity data used in the calculations**

Element	Species	Temperature of experimental determinations (K)	Source of activity data
In	$\text{InO}_{1.5}$	1873	Norris (2016)

Sn	SnO ₂	1773-2173	Righter et al. (2017)
Sb	SbO _{1.5}	1873	Norris (2016)
Te	TeO	1573	Johnston et al. (2010)
I	I	N/A	FactSage™ (Slag F)*

382

383

384 **Table 4 Parameterization of activity coefficients as a function of temperature according**
 385 **equation (9) for two chemical compositions of the system**

Composition	In	Sn	Sb	Te	I
Basalt	A = -22195	A = 7527.7	A=5050.28	A=1415.7	A=934.15
	B=0	B = 4.5393	B=0	B=0	B=4.8917
Granodiorite	A=-30055	A = 7527.7	A=-7025.68	A=1415.7	A=-1260.2
	B=0	B = 4.5393	B=0	B=0	B=0.8657

386

387

388 For In and Sb, twenty-four experiments reported in Norris (2016) were used to calculate the
 389 parameterization of the activity coefficients as reported in Table 4. For tellurium and tin, there
 390 is a more limited set of experiments (Johnston et al., 2010) or limited variations in the chemical
 391 composition of the silicate (Righter et al. 2017) and thus no dependence on composition was
 392 assumed as shown in Table 4.

393 A second step (if sufficient data is available) was to parameterize the variations in activity
 394 coefficients as a function of the various chemical compositions for the systems studied here.
 395 This was done by using the model proposed by O'Neill and Eggins (2002), which can be
 396 described by the following equation valid for a given temperature:

$$397 \quad \ln \gamma_i = \sum_{j=1}^n \sum_{k=1}^j a_{ij} X_j X_k \quad (11),$$

398 where i and j refer to the chemical components listed in Table 2. It is considered here that the
 399 trace elements have little influence on each other in the silicate mixtures. This summation
 400 implies cross-terms ($X_j X_k$) and quadratic terms such as X_j^2 .

401

402 **7. Results of condensation temperature calculations**

403

404 *7.1. Reference calculations without solubility or with ideal mixing*

405 For the sake of comparison with more complete calculations (as detailed below), we first
406 produced simplistic thermodynamic simulations. As an initial experiment, we consider no
407 solubility of In, Sn, Sb, Te and I in the silicate melt. In this case, the condensation of these
408 elements is implicitly controlled by the condensation of pure compounds, i.e. indium oxide
409 (In_2O_3), cassiterite (SnO_2), cervantite (SbO), tellurite (Te_2O_3), and lautarite $\text{Ca}(\text{IO}_3)_2$ (this species
410 is the first to be saturated among all other species present in the database). Their vapor
411 pressures were calculated at a pressure of 50 bars for a basaltic composition and their
412 condensation curves are shown in Figure 3. The condensation temperatures for In, Sn, Sb, Te
413 and I are given in Table 5. Second, one can also assume that each of these elements can form
414 an ideal mixture with the silicate melt assuming that the activity coefficients are equal to 1
415 (Henry activity coefficient for infinite dilution). The resulting condensation curves are depicted
416 in Figure 4, also at a pressure of 50 bars for a basaltic composition. They are significantly offset
417 compared with the previous calculations (Fig. 3). The condensation temperatures for In, Sn,
418 Sb, Te and I are given in Table 5. These results show that assuming ideal dissolution in a silicate
419 melt will produce higher condensation temperatures than for the case of pure substances. As
420 we shall see below, since the solution is not ideal, these condensation temperatures have to
421 be further refined.

422

423 *7.2. Condensation in conditions relevant to underground nuclear explosion conditions*

424 The activity coefficients determined with the methods presented above were used to
425 calculate equilibrium vapor pressures and condensation temperatures relevant for the P-T
426 conditions and bulk chemical composition of an underground nuclear cavity. The
427 corresponding condensation temperatures are given in Table 5. The condensation curves
428 calculated at four discrete pressures (1-10-50-100 bar) are shown in Figures 5 and 6 for the
429 basalt and granodiorite compositions given in Table 2. The calculations were carried up to a
430 temperature of 4500 K. For the pressures above 50-100 bars, the initial fraction in the vapor
431 phase is in some cases slightly below one, indicating that the condensation has started at a
432 temperature slightly higher than 4500 K. However, these high pressures and temperatures
433 correspond only to a short transient state of the system, when there is little time for elemental
434 fractionation due to the half-lives of the considered elements (Plompen et al., 2020). It should
435 be mentioned here that the calculation of activity coefficients was not extrapolated beyond

436 4500 K, which means that the upper limit of the pressure in our calculations is approximately
 437 100 bars. Iodine condenses at a much lower temperature than the other elements and it
 438 remains a volatile element until 500-600 K with only limited solubility in the silicate melt.
 439 Iodine finally condenses as lautarite ($\text{Ca}(\text{IO}_3)_2$), which suggests that there is only limited
 440 partitioning of I in the silicate or oxide minerals that are saturated at these temperatures such
 441 as feldspar, quartz, sphene or rutile (see also Musselwhite, 1995).

442
 443 Figure 7 shows the variation of condensation temperatures with pressure for the granodiorite
 444 (Figure 7a) for the basalt (Figure 7b). As expected, there is a general increase in condensation
 445 temperature with pressure but this increase depends on the condensation reactions. In
 446 addition, the condensation of each element takes place over a wider range of temperatures
 447 than for a pure element. This can be interpreted as resulting from the presence of solutions
 448 (here a silicate liquid) as well as from the vapor speciation of each element that changes with
 449 temperature.

450 The condensation temperatures are distinct from the boiling temperature of pure compounds
 451 used in the study of Carrigan et al. (2020) and Sun et al. (2021) to describe condensation of
 452 the elements of interest. For example, at 1 bar, Sn is more volatile than In in a silicate melt,
 453 while it is the reverse for metallic indium and metallic tin (see Table 1 for the boiling
 454 temperature of the pure metals). Last, at the same pressure of 1 bar, the condensation
 455 temperature for a given element can be offset by a few to several hundreds of kelvins
 456 compared with the boiling temperature (for Sb, 2697 K (granodiorite) or 1640 K (basalt)
 457 instead of 1760 K for the boiling temperature of metallic antimony at 1 bar).

458
 459
 460 **Table 5 Condensation temperatures (kelvin) calculated for In, Sn, Sb, Te and I in a nuclear**
 461 **cavity at 4 pressure values for two host rock compositions**

Rock composition and pressure	In	Sn	Sb	Te	I
Granodiorite 1 bar	3407	2389	2697	1122	499
Granodiorite 10 bar	3869	2959	3107	1718	550
Granodiorite 50 bar	4101	3579	3475	1921	600
Granodiorite 100 bar	4159	3934	3645	2021	650

Basalt 1bar	3075	2250	1640	—	500
Basalt 10 bar	3445	2840	1800	—	550
Basalt 50 bar	3820	3526	2689	1940	600
Basalt 100 bar	3838	3930	2893	1970	649
Basalt 50 bar (pure substances)	2964	3637	2154	2144	578
Basalt 50 bar (ideal mixing)	1310	3627	1748	875	557

462

463 If one compares the condensation temperatures as a function of the chemical composition,
 464 one notices significant variations between the granodiorite and basaltic cases. For example,
 465 there is a 500 K offset for the Sb condensation temperature between the granodiorite and the
 466 basalt. This can be partly explained by the variation in activity coefficients that range between
 467 0.38 (basalt at 2000 K) and 2.0 (granodiorite at 2000 K).

468 The activity coefficients used in this study were derived from experimental studies and
 469 extrapolated to the relevant temperatures or chemical compositions, when available. These
 470 calculations could be improved by experimental measurements of activities for a range of
 471 temperatures and for the actual chemical compositions of the magma found after
 472 underground nuclear explosions. These activity measurements could be made thanks to a
 473 Knudsen Effusion Mass Spectrometer, as illustrated in Costa et al. (2017) who studied the
 474 vaporization of olivine which is a common silicate mineral found in basalts and mantle rocks.

475

476 **8. Potential caveats**

477 *8.1. Kinetic barriers to condensation: possible deviations from equilibrium calculations*

478 The condensation of a vapor has been studied from a theoretical and experimental viewpoint
 479 by physical chemists. Thus, the main parameters that control the kinetics of condensation are
 480 known (e.g., Hirth and Pound 1963; Mutaftschiev 2001). First, the initial step for starting
 481 condensation is to start the nucleation of a droplet or a crystal and this requires that the
 482 system must overcome the so-called nucleation barrier which represents the minimum energy
 483 to nucleate. This energy barrier depends on the level of oversaturation, i.e. the pressure of
 484 the species that condensate relatively to the equilibrium pressure or vapor pressure. It is well
 485 known that the greater the overpressure, the smaller this energy barrier. Second, the
 486 nucleation is considerably eased up by the presence of a substrate. The substrate could consist
 487 of the host rock or of aerosols that may form in the vapor phase. In this case, the energy

488 barrier for nucleation can be lowered by a factor that depends on the wettability of the
489 condensing liquid onto the substrate.

490 Independently of these considerations, the rate of condensation dn_i/dt onto a surface can
491 be described by the Hertz-Knudsen equation that illustrates directly the dependence of
492 condensation rates on the degree of oversaturation (Hirth and Pound 1963):

$$493 \quad \frac{dn_i}{dt} = \frac{\gamma_i P_i}{\sqrt{2\pi m_i RT}} \left(1 - \frac{P_{i,sat}}{P_i}\right) \quad (12)$$

494 γ_i is the condensation coefficient, P_i and $P_{i,sat}$ are the partial pressure and the saturation
495 pressure of species i , m_i , its mass. This equation also shows the importance of a second
496 parameter, which are the condensation coefficients. This parameter is directly linked with the
497 probability for a vapor species to actually condensate once it hits a liquid or solid surface. As
498 this parameter can be considerably lower than one, this means that the condensation rate can
499 be significantly lower than what is predicted with the common assumption of a γ_i value equal
500 to 1. In a comprehensive model of condensation from a vapor formed in a nuclear cavity, all
501 these parameters would need to be taken into account.

502

503 *8.2. Potential complications arising in the conditions of underground nuclear explosions*

504 As stated above, our calculations were done for a closed system evolving in chemical
505 equilibrium at fixed pressure with a fixed amount of volatile species such as water. Real
506 systems could exhibit additional complexities, which could produce significant deviations
507 compared with what was calculated here. These potential complications are briefly reviewed
508 here based on existing literature.

509 In the initial stages following the explosion, the vapor in the cavity can reach temperatures
510 that are higher than the country rock at the boundary of the cavity, as described in Chapin
511 (1970). Our calculations therefore do not apply to this stage. However, as explained in Chapin
512 (1970), there is a rapid cooling of the overheated vapor until thermal equilibration is reached.
513 Another issue that is particularly relevant regarding the more volatile elements among those
514 studied here is that the vapor could cool by radiative heat loss or adiabatic expansion into
515 fractured rocks outside the cavity. In this case, the system that we study should not consist of
516 magma + vapor, as one could consider that the vapor gets isolated from the magma. This
517 decoupling could take place at pressures of 30-50 bars (Higgins and Butkovich, 1967). Another
518 consideration that may play a role is that the diffusion timescale of the Xe precursors in the

519 magma might get slower as the temperature decreases. As shown in Figure 8a, for
520 temperatures below 3000-3500 K, the diffusion length scales of Te, Sb and Sn in a basaltic melt
521 decrease considerably, which argues against equilibration between vapor and magma in this
522 case. To further consider the effect of vapor isolation, we have calculated in the case of the
523 basaltic composition at 50 bars, the condensation temperatures of In, Sn, Sb and Te from an
524 isolated vapor produced at 3500 K. The results are plotted in Figure 8b and show that there
525 can be a significant shift in the condensation temperature corresponding to this situation. This
526 calculation illustrates that it is possible to take into account such a complication, provided a
527 reasonable scenario is considered.

528 The heating of the cavity walls can lead to the vaporization of water that can then mixed with
529 the existing vapor inside the cavity (e.g. Chapin 1970). In this case, the water content of the
530 initial vapor could exceed the bulk composition of the rock (i.e. basalt or granodiorite in our
531 cases). In order to consider the effect of this excess water on the condensation temperatures,
532 we have calculated the condensation temperature by increasing by a factor of 2 and a factor
533 of 10 the amount of water contained in the basaltic composition (Table 2). The results
534 obtained for the condensation temperature are shown in Figure 9. By increasing the bulk
535 water content, the condensation temperatures are significantly lowered, especially when the
536 water content is multiplied by a factor of 10. Again, this illustrates that our thermodynamic
537 calculations can be adapted to specific conditions in view of a more comprehensive modeling
538 of condensation in a nuclear cavity.

539 It should be emphasized here that the processes that take place right after the explosion (until
540 radioxenon release to the atmosphere) are the most significant in determining the relative
541 proportion of xenon isotopes (note that U and Pu have similar radioxenon fission yields), as
542 during atmospheric transport the xenon isotope abundances are only controlled by
543 radioactive decay.

544

545 **9. Implications of condensation on radioxenon**

546 As temperature and pressure are decreasing in the nuclear cavity, the condensation of In, Sn,
547 Sb, Te and I, the successive precursors to radioxenon, has a direct consequence on the final
548 accumulation of radioxenon, since the cooling rate can be fast relative to the escape rate of
549 xenon. For a quantitative estimate of these effects, one would need a precise knowledge of
550 the timescale leading to the fractionation of these precursors from the original gas phase. This

551 could be obtained by coupling the condensation calculations, the cooling history of the cavity
552 and its fractured chimney and the decay chains leading to radioxenon. As the thermo-chemical
553 evolution of nuclear cavities can be complex (see section 8.2), various scenarios should be
554 taken into account. Such an approach goes well beyond the scope of the present study and
555 will be the subject of future work.

556 In the meantime, our calculations can be used to illustrate the consequences of differential
557 condensation from a qualitative viewpoint. It is shown here that indium should rapidly be lost
558 by condensation upon cooling, due to its condensation temperature higher than 3000 K (Table
559 5). However, the half-lives of ^{131}In , $^{131\text{m}}\text{In}$ and ^{133}In are 0.28s, 0.35s and 163 ms, respectively,
560 which means that their lifetimes are too short relative to the cooling timescale in the 3000-
561 4000 K range (>30 s, Chapin 1970) to be affected by condensation. Had we used the boiling
562 temperature of pure In (2350 K) as in Carrigan et al. (2020), the conclusion would have been
563 identical since in this temperature range the cooling is even slower, which leaves no time for
564 condensation before radioactive decay.

565 The situation is different for the Sn isotopes ^{131}Sn , ^{133}Sn and ^{135}Sn , with half-lives of 56 s, 1.45
566 s and 520 ms, respectively. In this case, there could be an effect on ^{131}Sn with the consequence
567 that there would be a smaller in-growth of ^{131}Xe due to partial condensation before decay
568 (this effect could be enhanced by the large temperature interval for Sn condensation, e.g.
569 Figure 6). Similarly to In isotopes, ^{135}Sn would rapidly decay before condensation could take
570 place. The cases of Sb and Te are more difficult to assess qualitatively as the condensation
571 temperatures are lower and the half-lives of intermediate isotopes are longer. Thus,
572 deciphering the relative contribution of condensation and decay would require quantitative
573 modeling. For example, the half-life of ^{131}Te (25 min) combined with a condensation
574 temperature of 2040 K at 50 bars suggests that over that timescale both the temperature and
575 pressure in the cavity should have dropped significantly (e.g. Chapin 1970) to a level where
576 condensation of Te would compete with its decay.

577 Overall, our results suggest that a reliable estimate of the quantity of xenon available for
578 migration out of the nuclear cavity and the relative abundances of the radioactive xenon
579 isotopes used as signatures for underground nuclear testing should not ignore: (i)
580 condensation of the radioxenon precursors, (ii) determination of the true condensation
581 temperatures based on actual thermodynamic data, (iii) the deviation of the condensation
582 temperatures from boiling temperatures and from thermodynamic ideality, (iv) the

583 dependence of condensation temperatures on the host rock composition (and its water
584 content), (v) the dependence of condensation temperatures on pressure in rapidly evolving
585 environments such as underground explosions (vi) the role of vapor isolation, if that process
586 can be considered to have been effective.

587 In the longer term, by combining the thermodynamic properties of elements (as derived in
588 this study) with a physical model for the thermal evolution of the cavity (e.g. Chapin, 1970),
589 as well as a reactive transport model for the vapor above the nuclear cavity (Sun and Carrigan,
590 2016; Pazdniakou et al., 2022), one should be able to obtain a more realistic picture of the
591 processes happening after the explosion. This type of information should provide better
592 estimates of the radionuclide source term potentially emitted to the atmosphere, thereby
593 providing a better diagnostic tool than previous more simplistic models.

594

595 **10. Conclusions**

596 This study highlights that thermodynamic modeling is essential for a proper evaluation of the
597 effect of condensation of In, Sn, Sb, Te and I in a nuclear cavity following an underground
598 nuclear explosion. A model that properly predicts the behavior of these elements must include
599 realistic values of their activity coefficients in silicate melts of given compositions and take
600 into account the variation of these parameters over a large range of temperatures and
601 pressures. If these parameters are not accounted for, there can be large deviations by several
602 hundreds of kelvins in the condensation temperature of the elements considered here.
603 Furthermore, condensations of some radionuclides are shown to occur over a temperature
604 range as large as 2000 K, in strong contrast with the often referred to Heaviside function.
605 These determinations of condensation temperatures and vapor pressure evolutions can also
606 take into account potential complications arising in the conditions of underground nuclear
607 explosions, such as to the effect of vapor isolation from the magma, or addition of extra water
608 from devolatilization of the country rock, or even the kinetic barriers to condensation.

609 Since the radionuclides considered here are the precursors of radioxenon (^{131m}Xe , ^{133}Xe ,
610 ^{133m}Xe , ^{135}Xe) used in the detection and discrimination of underground nuclear testing, an
611 incorrect estimate in the condensation behavior of these elements could lead to slanted
612 estimates of the source term used in atmospheric transport modeling to interpret data from
613 the CTBT international monitoring system. The reader is referred to Ringbom et al. (2014) for
614 a worked example of the interpretation of such data.

615 In addition, as condensation varies with temperature, pressure and the bulk chemical
616 composition of the system, a heterogeneous spatial distribution of the condensed
617 radionuclides is expected in the nuclear cavity, notably among the variety of the melts
618 produced over time (e.g., Boardman et al., 1964, Schwartz et al., 1984). This could have a
619 strong impact on the nature and quantity of the radionuclides available for migration,
620 particularly when estimating the hydrologic source term (e.g., Tompson et al., 2011).
621 Thanks to our determinations of condensation temperatures and vapor pressure in relevant
622 conditions, it should be possible to give better estimates of the fluxes of the precursor isotopes
623 to radioactive xenon potentially emitted from nuclear explosions as a function of the pressure
624 and temperature of the system. As mentioned above, the dynamics of cavity formation and
625 evolution may complicate the simple picture of a closed system condensation. Nevertheless,
626 our work provides more realistic parameters that can be used to extend earlier studies based
627 on pure substances, allowing better modeling of these complex systems.

628

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Figure captions

Figure 1 Radioactive decay chains for the 131, 133, and 135 isobars leading to xenon. Horizontal arrows denote isomeric transitions, with the superscript m for the metastable nuclide; other arrows denote β^- decay. Numbers on arrows indicate the half-lives with the following units: second (s), minute (min), hours (hr) days (d), millions of year (Myr). Data are taken from the joint evaluated fission and fusion nuclear data library 3.3 (Plompen et al., 2020). Cadmium (Cd) is neglected in this condensation study owing to its very short half-life, as well as the daughter products of xenon (Cs and Ba) as their trapping in the magma has no effect on the Xe inventory.

Figure 2 Calculated activity coefficient of SnO_2 in a silicate melt based on metal-silicate partition coefficient from Righter et al. (2017).

Figure 3 Condensation curves for a basaltic composition at 50 bar, volatility controlled by the pure substances, TeO_2 , SnO_2 , In_2O_3 , SbO_2 , $\text{Ca}(\text{IO}_3)_2$. The fraction in the vapor is calculated using the ratio of the molar abundance in the vapor to the initial molar abundance in the bulk system.

Figure 4 Condensation curve for a basaltic composition at 50 bar assuming an ideal mixture between In_2O_3 , SnO_2 , SbO_2 , TeO_2 and $\text{Ca}(\text{IO}_3)_2$ and the silicate melt ($\gamma_{\text{MxOy}} = 1$).

Figure 5 Condensation curves of I, Te, Sb, Sn, and In for a granodiorite composition at (a) 1 bar, (b) 10 bar, (c) 50 bar and (d) 100 bar, as labeled on the diagrams.

Figure 6 Condensation curves of I, Te, Sb, Sn, and In for a basalt composition at (a) 1 bar, (b) 10 bar, (c) 50 bar and (d) 100 bar, as labeled on the diagrams.

666 Figure 7 (a) Variations of the condensation temperature (K) as a function of pressure (bars) for
667 a granodiorite composition. (b) Variations of the condensation temperatures (K) as a function
668 of pressure (bars) for a basalt composition.

669
670 Figure 8 (a) Diffusion length scales of Te and Sb in a basaltic melt as a function of temperature.
671 Diffusion coefficient data from MacKenzie and Canil 2008. (b) condensation temperatures for
672 In, Sn, Sn and Te in the case where vapor is isolated from the magma at 50 bars and 3500 K.
673 The curves with a dashed line (identical color code) represent the condensation for the case
674 with no vapor isolation (similar to Figure 6 at 50 bar).

675
676 Figure 9 Condensation temperatures calculated for In, Sn, Sb and Te at 10 bars for the basaltic
677 composition with a water content increased by a factor of 2 (short dash line) and a factor of
678 10 (long dash line) compared to the original one (solid line) as given in Table 2.

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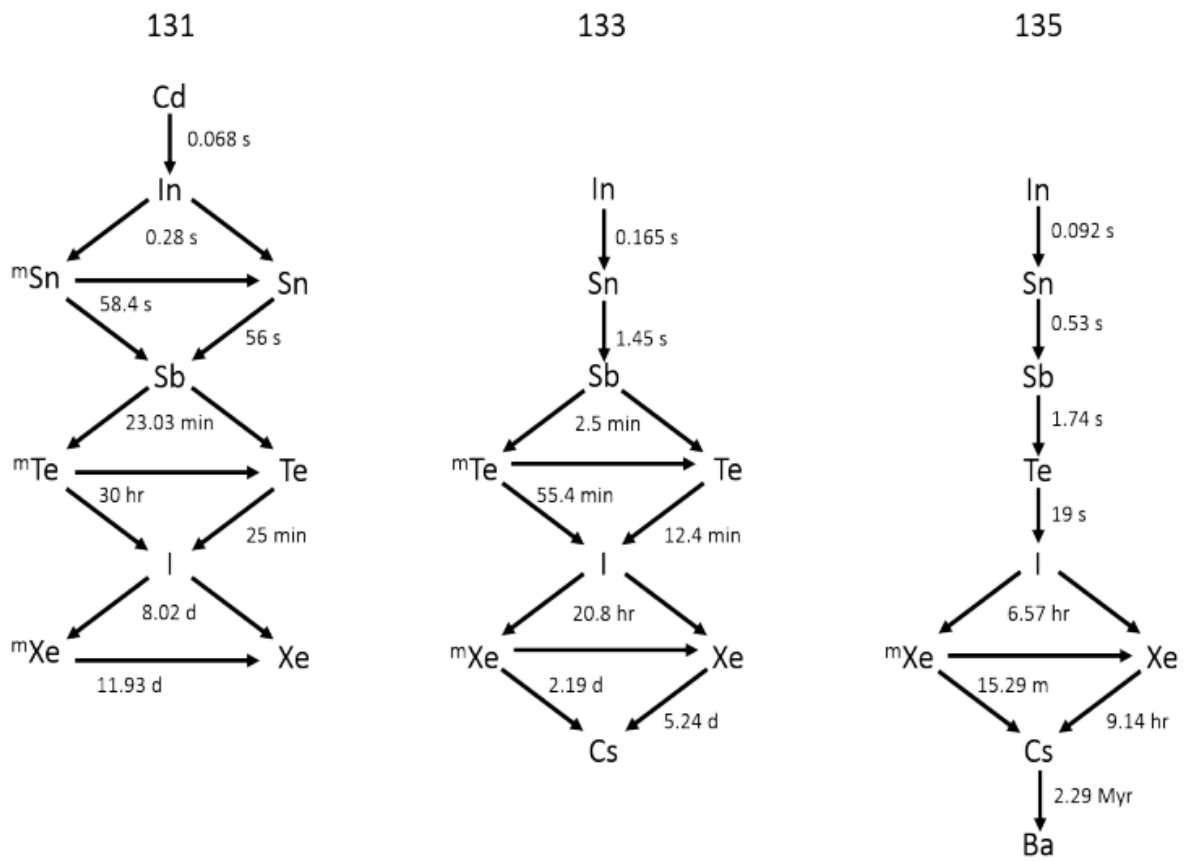
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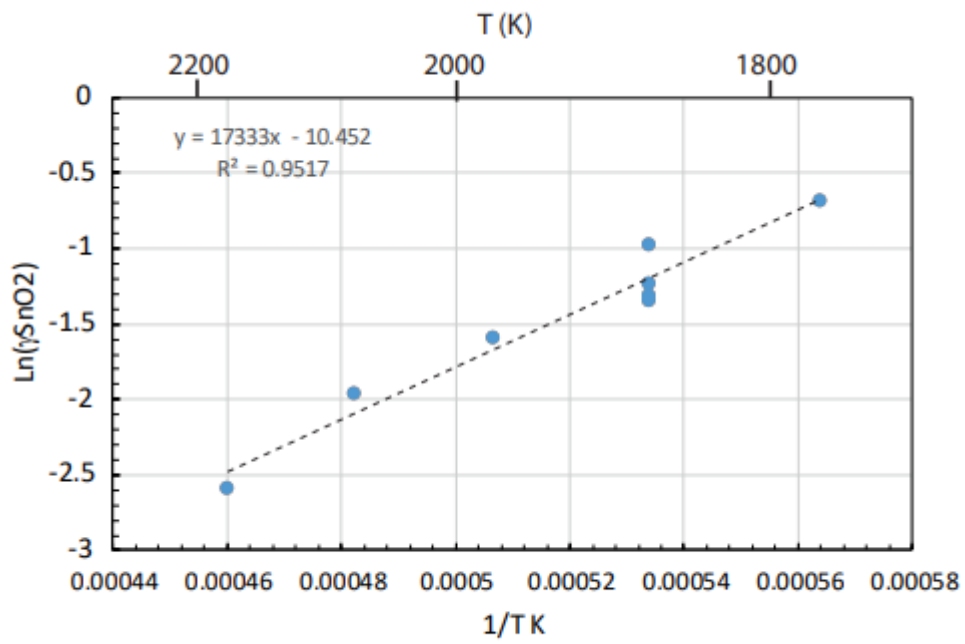
938 Figure 1



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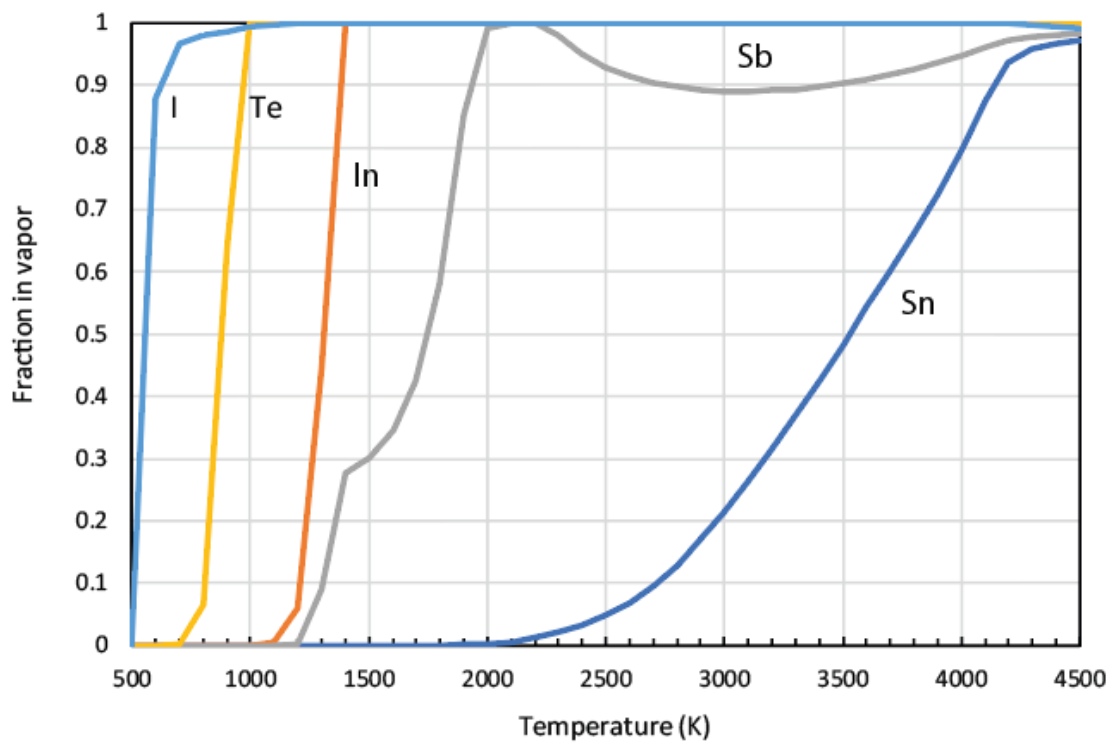
941 Figure 2



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944 Figure 3

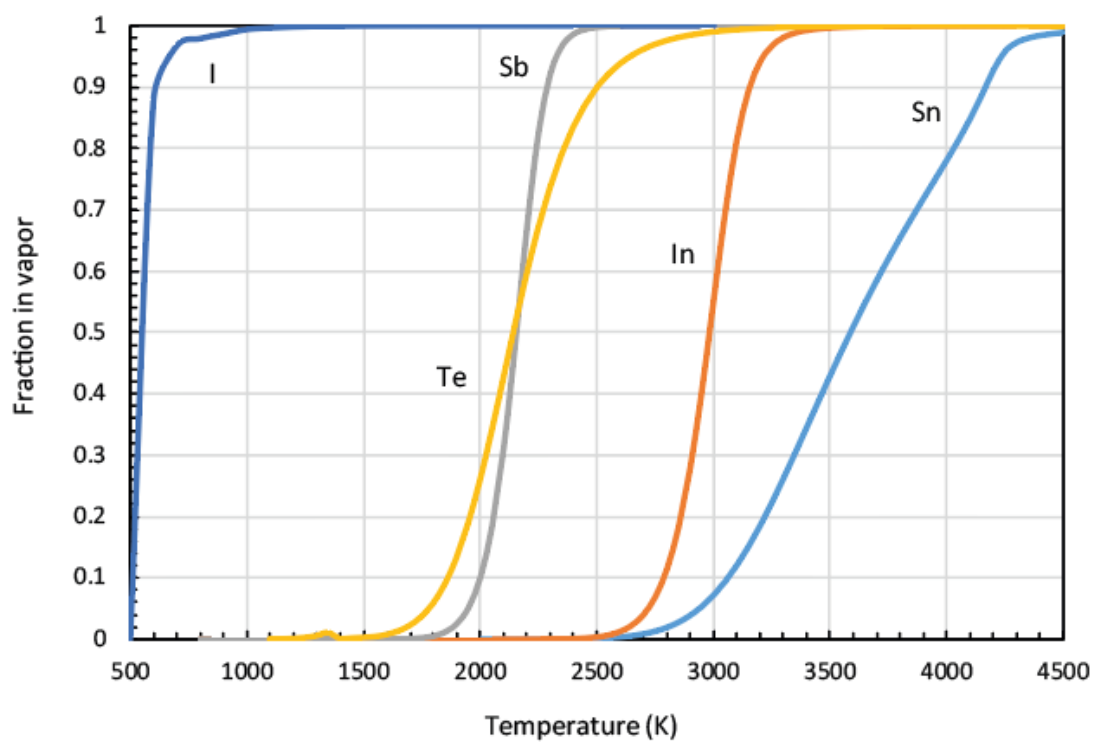


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947 Figure 4

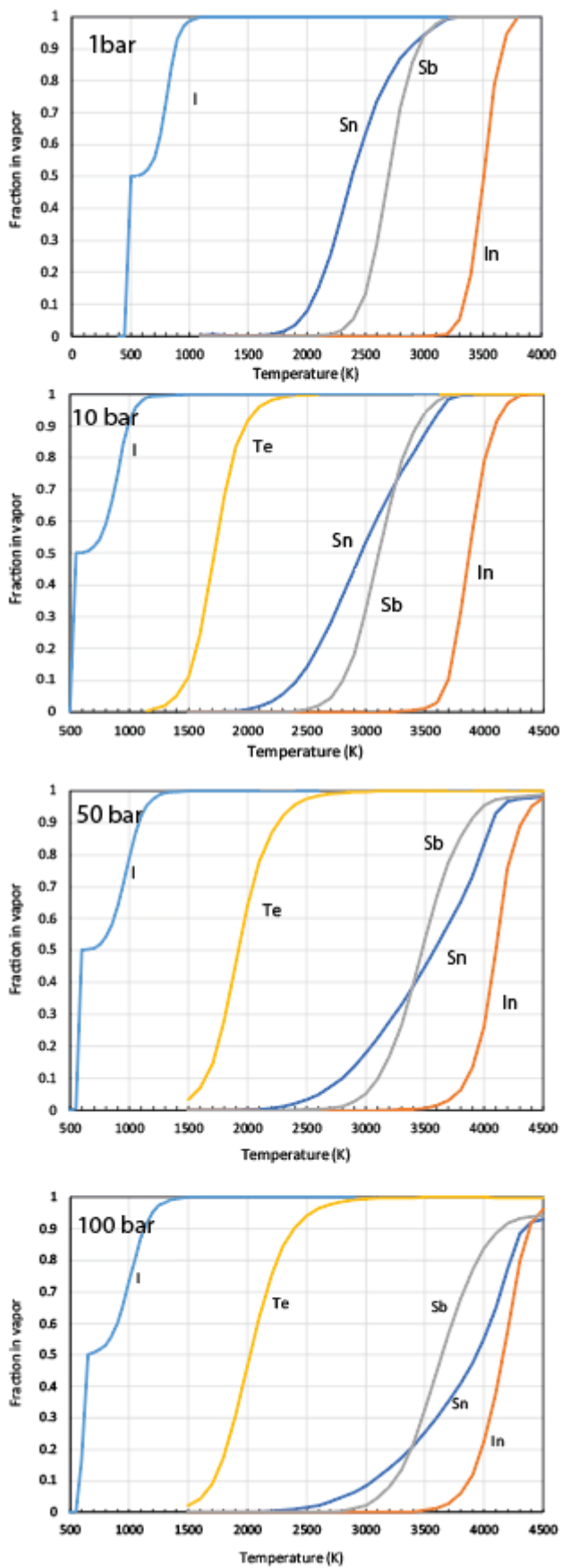
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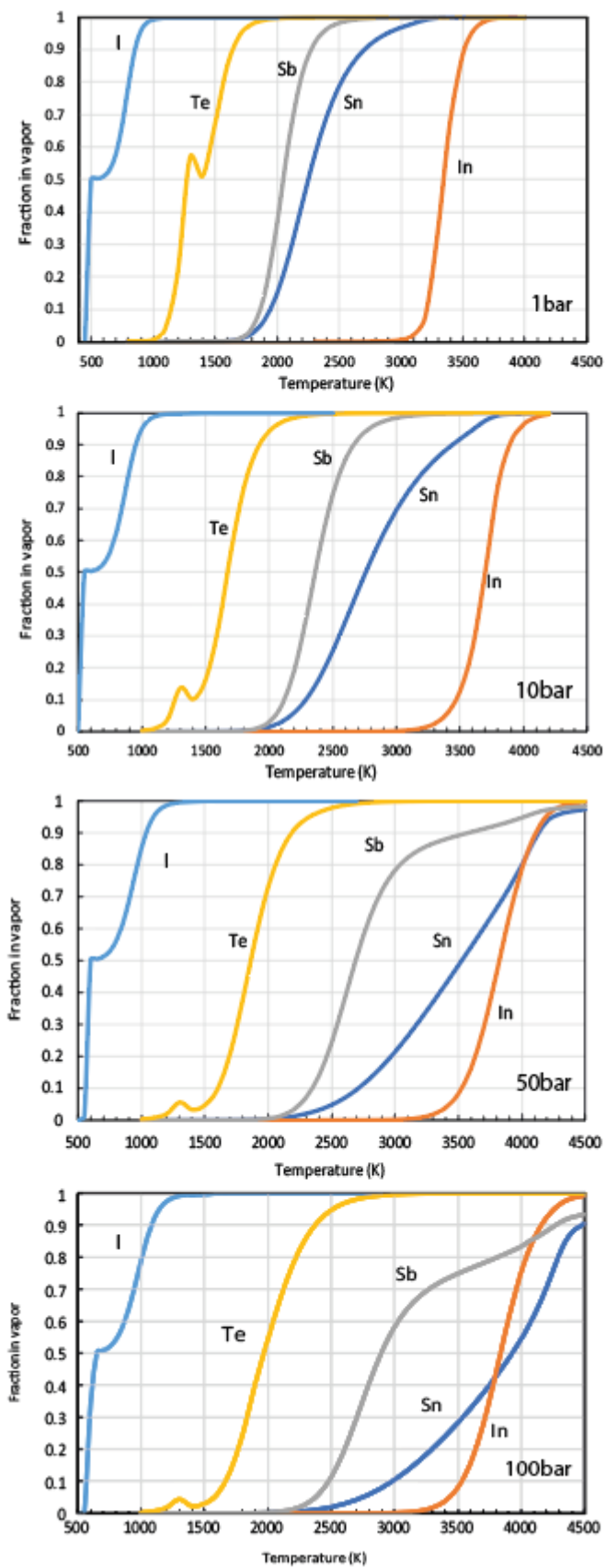
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951 Figure 5



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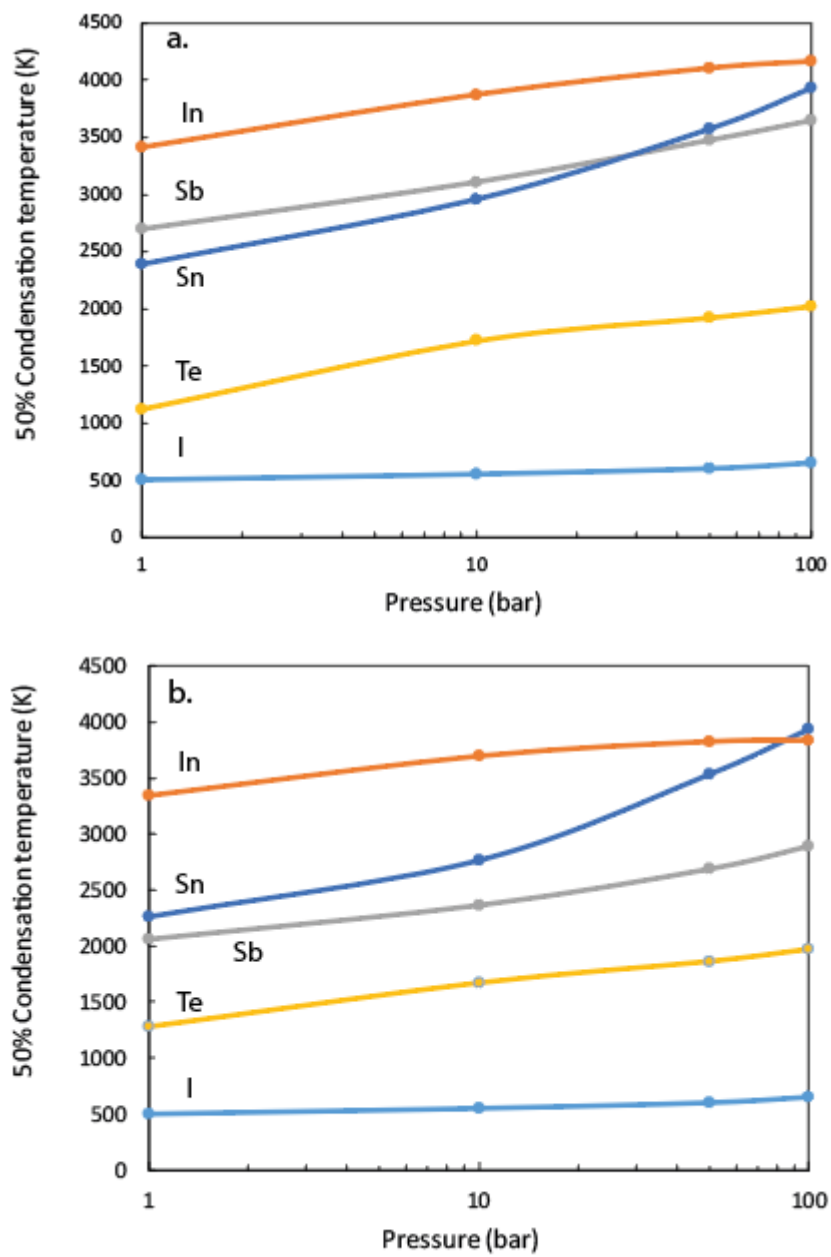
953 Figure 6



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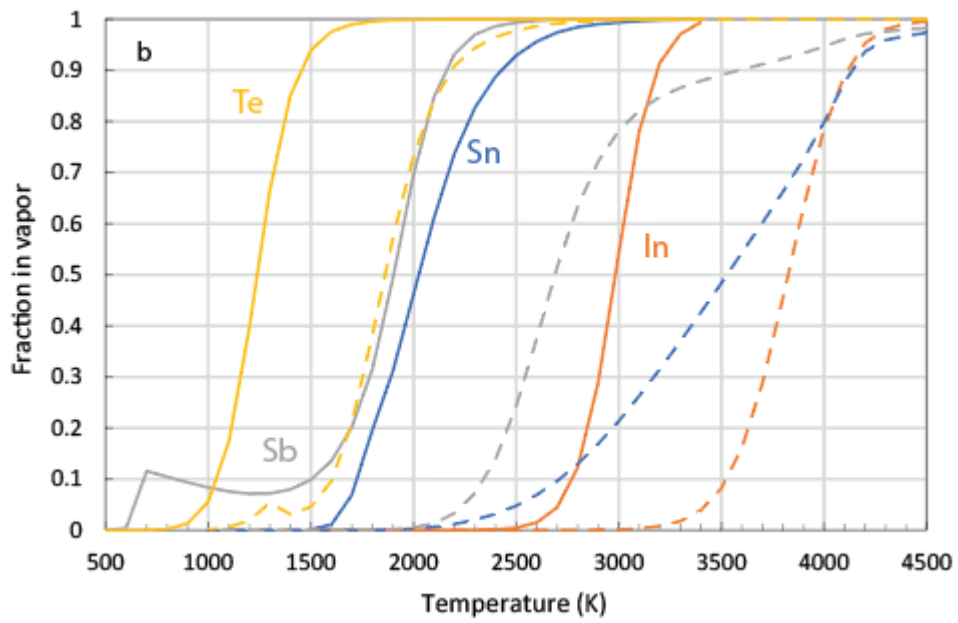
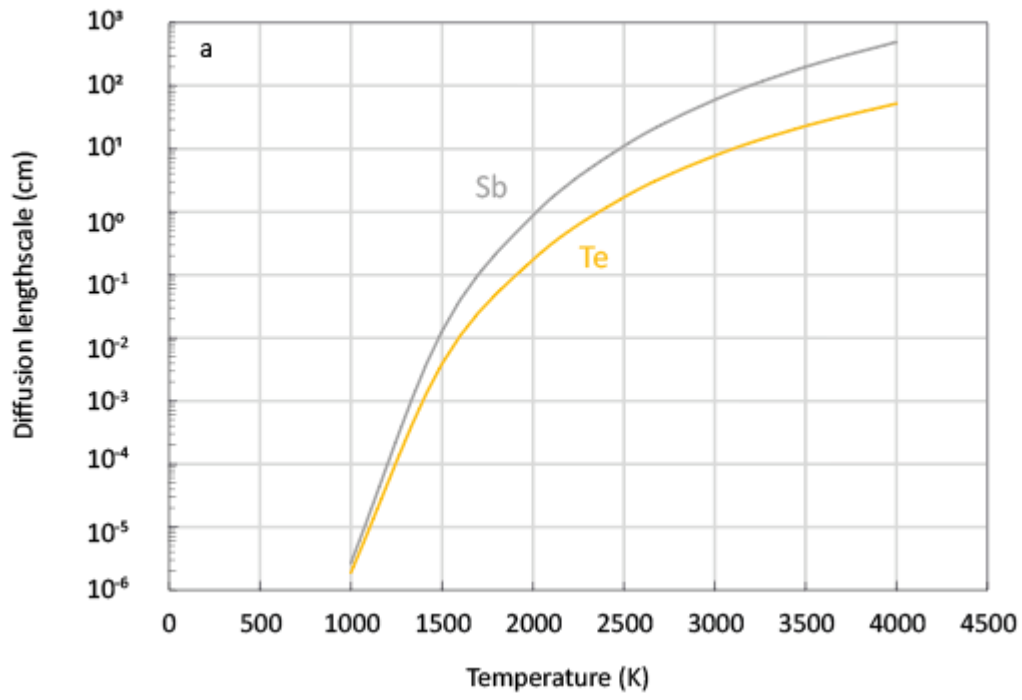
956 Figure 7



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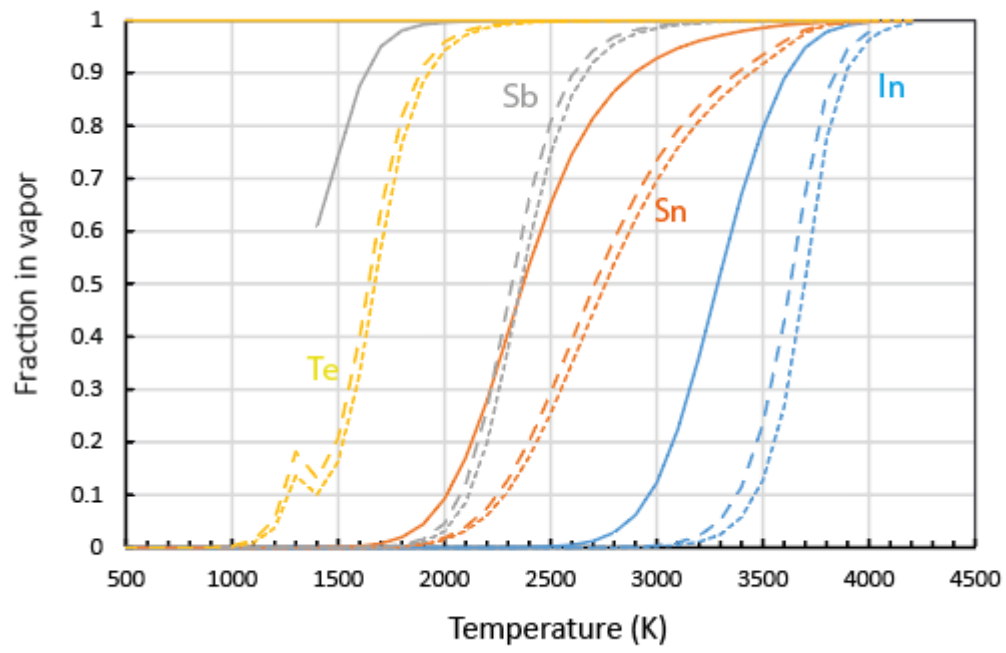
959 Figure 8



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962 Figure 9



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