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

pure compounds often used as indicators of their volatility. For some precursory elements such as tin, the often-considered Heaviside function represents an oversimplification of the concept of condensation temperature, as condensation occurs over a temperature range as large as 2000 K. This results from the speciation of the elements in the gas phase mainly driven by the formation of oxides. Condensation also strongly depends on pressure while it moderately depends on the bulk chemical composition of the system. This study shows the importance and complexity of the condensation process following underground nuclear explosions. It also shows how thermodynamic computations allow the prediction of the quantity and the relative proportions of radioactive xenon isotopes in the gas phase in the presence of magma, before their potential emission to the atmosphere. Better detection, discrimination and understanding of underground nuclear explosions should arise by taking into account the fractionation resulting from the condensation of the radionuclides producing radioxenon in nuclear cavities.

40

41

42 1. Introduction

43 The atmospheric detection of four radioactive isotopes (131m, 133m, 133 and 135 where m is for metastable) of xenon (Xe), altogether referred as radioxenon, possibly released at the 44 45 ground surface following an underground nuclear explosion is a means for the verification of the Comprehensive nuclear Test Ban Treaty – CTBT – (UNODA, 1995; Carrigan et al., 1996; 46 Hourdin and Issartel, 2000). Owing to many complex phenomena that occur after the 47 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; Pazdniakou et al., 2022) as well as the existence of an atmospheric background radioxenon signal not derived from underground nuclear 54 55 explosions (Achim et al., 2016). One overlooked process that controls the availability of radioxenon is the partitioning of its precursory elements between the melt and gas phases in 56 57 the nuclear cavity immediately after the explosion (Carrigan et al., 2020, Sun et al., 2021, 2022). 58

An underground nuclear explosion vaporizes the materials surrounding the detonation point and further melts the adjacent rocks (Taylor 1973). Upon cooling, condensation of the vaporized matter and melting of the cavity walls and debris leads to the production of a liquid whose composition depends on the surrounding rocks, while the material added by the nuclear device is comparatively small. As a result of nuclear fission, radioxenon is produced by 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 xenon (Xe). Therefore, depending on the cooling history of the nuclear cavity together with 67 the short-lived existence of the nuclides controlled by the decay chains, the precursory 68 elements may condense into the magma or on the colder surfaces of rocks (cavity walls or 69 chimney rubbles) before radioxenon may have escaped the nuclear cavity and started 70 71 percolation through the fractured geological media towards the atmosphere. If condensation is sufficiently rapid compared to decay, the production of the various radioxenon isotopes in 72 73 the vapor phase of a nuclear cavity can be altered.

Thus, in order to make more accurate predictions about the composition of the Xe isotopes 74 possibly emitted to the atmosphere, it is necessary to know whether the precursory elements 75 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 gas phase. In this study, we have determined the equilibrium conditions of the vapor-magma 78 system from which we deduced condensation temperatures and vapor pressures for the 79 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 energy is deposited, about 70 tons (per kiloton (kT) of explosive energy) of material reaches 86 87 temperatures large enough to complete vaporization (Butkovich 1974a). Beyond this zone of full vaporization, the deposited energy is sufficient to fully melt in the order of 1000 tons of 88 89 material (per kT of explosive energy), depending on the initial density of the rock (Butkovich 1974b). The vapor that is produced by the explosion expands and forms a cavity containing 90 both melt and vapor. The volume of the cavity is controlled by the depth of the explosion, the 91 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 pressure and temperature as the initial energy is dissipated in the geological medium. This 95 corresponds to an early stage depicted in Figure 7 of Schwartz et al. (1984) where the magma 96

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 gives enough time for thermal and chemical equilibrium to take place between the magma 99 and the gas phases, relative to the timescales of the radioxenon decay chains considered here. 100 101 The system cools relatively rapidly and ultimately forms magmatic glass commonly analyzed for its radioactive content. Most of the budget of refractory fission products is observed to be 102 103 contained in the magma (Borg 1975; Smith et al. 1996; 2003) rather than with the rubble that piles up at a distance from the magma found at the bottom of the cavity. This is a strong 104 105 indication that the refractory elements that must have been initially vaporized upon the explosion were mostly condensed in the magma, rather than being dispersed in the 106 107 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 magma. Thus, it seems reasonable to assume that at least in the beginning, there is a thermal 110 111 and chemical equilibrium between the vapor phase and the magma as assumed in what 112 follows.

113

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 since it depends directly on the ambient pressure. For a pure substance, in the case of a liquid-118 119 vapor equilibrium, the condensation temperature is only defined at a given pressure and corresponds to a point of the liquid-vapor curve in a P-T phase diagram. In this case, the 120 121 saturation vapor pressure at equilibrium is defined by the Clausius-Clapeyron law, which is expressed for a vapor-liquid phase change. In the case of multi-component systems, such as 122 the one studied here, at a given pressure, there is a range of temperatures for which the 123 element considered will coexist in vapor phase and in liquid phase. The condensation curve is 124 125 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 temperature corresponding to an equal partitioning (50%, expressed in number of moles) 127 between the condensed phase and the vapor phase. 128

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

144

145 Table 1 Condensation temperatures determined for cosmochemistry and boiling

Elemen	t Condensation to	emperature (K, at 10 ⁻⁴ atm)	Boiling temperature (K, at 1 atm)		
	Lodders (2003)	Wood et al. (2019)	Lide (1990) and reference therein		
In	492	536	2350		
Sn	604	704	2876		
Sb	890	979	1860		
Те	665	709	1261		
I	535	390	457		

146 temperatures

147

148

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

Depending on the condensation reaction describing the equilibrium between the vapor and liquid phase, the effect of oxygen fugacity can play a key role on volatility. This was for example demonstrated in the study of Ebel and Grossman (2000) who simulated conditions where the mass fraction of solid (mostly oxides) increased relative to H₂-dominant gas, which was equivalent to increasing the oxygen fugacity. One observes that the condensation temperatures of elements are highly dependent on this O₂ fugacity but this earlier work did not include the trace elements (In, Sn, Sb, Te and I) that are the focus of the present study.

The experimental studies of Norris et al. (2017) and Sossi et al. (2019) have further illustrated the dependence of oxygen fugacity for trace elements but could not determine the corresponding condensation temperatures and vapor pressures for these elements due to non-equilibrium conditions of their experiments. For most trace elements dissolved in an oxide melt, the condensation temperature increases with oxygen fugacity (f_{O_2}). This can be understood if one writes the vaporization reaction of a metallic oxide (MO_{melt}), as:

163 $MO_{melt} \leftrightarrows M_{gas} + \frac{1}{2}O_2$

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

172

171 **5. Thermodynamical approach**

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

The trace elements (In, Sn, Sb, Te and I) which are the focus of this study are generated as fission products from the nuclear explosive and they initially partition in the vapor phase 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 postexplosion pressure and temperature conditions. The temperature and pressure conditions are 177 in a transient regime with variable time constants which depend on the energy initially 178 released during the explosion and later dissipated in the geological medium. The range in 179 pressure (orders of magnitude of hundreds of bar to 1 bar, considered from the moment the 180 181 chimney is formed) and temperature was chosen to cover the typical range reported in the literature on these topics (e.g. Chapin 1970; Butkovich 1974a). Model curves depending on 182 183 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

(R1)

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. An additional feature that one should bear in mind is that the volatility of elements will not 187 only depend on the thermodynamics but also on the kinetics, both of evaporation and 188 condensation, and we assumed for the sake of simplicity that chemical equilibrium was 189 reached. Some of these aspects are discussed below in section 8.1. By lowering the 190 191 temperature at a given pressure, the elements are progressively condensed in the liquid phase starting with the most refractory to the most volatile. 192

As the relevant thermodynamic data were not available for temperatures greater than 2500
K, the thermodynamic parameters were extrapolated assuming that the parameterization
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 in Table 2, a granodiorite and a basalt. These chemical compositions are of interest because 198 they correspond to two extreme compositions typical of terrestrial rocks likely to be observed 199 200 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 Mururoa basalt is taken from Dupuy et al. (1994). The In, Sn, Sb, Te and I contents are fixed 208 209 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 contribution to each of these elements, considering conservatively 10⁻² mol of each isotope 211 for a 1 kT explosion and 400 kg of melt (Sun et al., 2014; Carrigan et al., 2020). Hence, the 212 213 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.

- 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
AI_2O_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
H₂O	1.0	1.96

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

219 4.2. Thermodynamic database and calculations

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

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

$$G_{tot} = \sum_{j} \sum_{i} \mu_i^j n_i^j \tag{1}$$

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
$$G_{tot} = \sum_{j} \left(\sum_{k} \left(\mu_{k_0}^{j} + RT ln f_k \right) n_k^{j} + \sum_{l} \left(\mu_{l_0}^{j} + RT ln a_l \right) n_l^{j} \right)$$
(2)

237 where index k and i are for the vapor phase and condensed phases, respectively, and f_k and a_1 238 are the fugacity and activity of component k and il respectively, in phase j. This approach requires a knowledge of all the thermodynamic properties of all the species contained in the 239 vapor (i.e. their fugacities) and of the mixing properties of the liquid phase and of the solid 240 241 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 optimize the phase proportions to minimize the total Gibbs energy of the system. These 243 244 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 temperature and pressure, which is an important assumption whose validity is discussed in 246 Section 8.2. 247

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

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

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

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

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

267

268 6. Determination of activity coefficients

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

273

274

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

For iodine, it has been shown that the most of it is in the form of I⁻ (McKeown et al. Muller et al. 2014; Cicconi et al 2020) and that iodide is often associated with alkalis (Na and K essentially) or with calcium, which is consistent with the components present in the SLAG-F solution of FactSage[™]. Previous experimental studies (Musselwhite et al. 2000; Cicconi et al. 2019; Riley et al. 2014; Jolivet et al. 2020) focusing on iodine solubility have not determined directly the iodine activity in silicate melts and this would deserve dedicated experimental 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 of 1923 K. For Sb, there are several determinations of the activity coefficient of SbO_{1.5} in oxide 284 285 mixtures, including those given in Norris (2016). Mendoza et al. (2001) have determined the activity coefficient for SbO_{1.5} in CaO-FeO-SiO₂ mixtures as a function of the CaO content in 286 287 oxide melts and show variations of this parameter between 1.8 and 3.9 at 1573 K. These values are rather close to the range in activity coefficients given in Norris (2016) at 1923 K (0.11-8.9, 288 mean=2.3). Thus, we have used values from the experiments of Norris (2016) and the results 289 are given in Table 4. A Raoult activity coefficient of SbO_{1.5} equal to 1.14 at 1923 K was reported 290 291 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).

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

297

298 6.2. The

6.2. The case of tin: SnO versus SnO_2

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

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

- 313
- 314
- 315

$$SnO_2^{sil} \leftrightarrows Sn^{met} + O_2^{gas}$$
 (R3)

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

318
$$2Fe^{met} + SnO_2^{sil} \leftrightarrows Sn^{met} + 2FeO^{sil}$$
(R4)

319 Its equilibrium constant can be expressed as:

320
$$K = \frac{a_{Sn}^{met} a_{FeO}^{sil}^2}{a_{SnO_2}^{sil} a_{Fe}^{met}^2} = \frac{X_{Sn}^{met} X_{FeO}^{sil}^2}{X_{SnO_2}^{met} X_{Fe}^{met}^2} \cdot \frac{\gamma_{Sn}^{met} \gamma_{FeO}^{sil}^2}{\gamma_{SnO_2}^{sil} \gamma_{Fe}^{met}^2}$$
(4)

One can see that the equilibrium constant is a function of the parameter we are interested in (i.e. $\gamma_{SnO_2}^{sil}$). Thus, provided all the other parameters are known, one can express the activity coefficient of SnO₂ in the silicate melt as a function of the equilibrium constant *K* and the other parameters. First, this equilibrium constant can be calculated at the temperature of interest using the free enthalpies of formation of the pure compounds Fe, FeO, SnO₂ and Sn reported in thermodynamic tables (Barin 1995). The free enthalpies of formation of each reagent and product are used to calculate the free enthalpy of the reaction R4:

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

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

330
$$LnK = \frac{-\Delta^{R}G}{RT} = 2LnK_{f}^{FeO} + LnK_{f}^{Sn} - \left(2LnK_{f}^{Fe} - LnK_{f}^{SnO_{2}}\right)$$
(6)

The formation constants of SnO_2 and FeO can then be parameterized as a function of 1/T using the data of Barin (1995), with the formation constant of pure Sn and Fe being equal to zero, by definition. One obtains for SnO_2 (valid between 1300 and 1800 K):

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

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

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

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

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

The parameters X_{Sn}^{met} , X_{Fe0}^{sil} , $X_{SnO_2}^{met}$, X_{Fe}^{met} can be determined for each bulk composition of 339 the silicate melt in the metal-silicate experiments (as given in Righter et al. (2017) in the case 340 of Sn) while the activity coefficients of FeO in the silicate melt are known from the literature 341 (e.g., Wood and Wade 2013). The activity coefficient of metallic Sn in molten iron alloys can 342 343 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 by Righter et al. (2017) and are also given in a compilation by the Japan Society for the 345 Promotion of Science (1988). Since all the parameters of equation (8) can be calculated 346 347 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 melts. Thus, based on equation (8), one can determine from the above equations the values 349 of $\gamma_{SnO_2}^{sil}$ although this parameter has never been directly determined experimentally. 350

By using this methodology, we have calculated the activity coefficients for two series of experiments, one with a graphite capsule and one with an MgO capsule (Righter et al. 2017). 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 concentration of C in the metal) yield γ_{SnO2} activity coefficients ranging between 10⁻² and 10⁻⁴ 355 356 which are comparable to those obtained by Norris (2016) with experiments involving also graphite. However, these experiments do not correspond to the situation found in 357 underground nuclear explosions where the C level of the environment is rather low for the 358 rock compositions studied here. We contend that an uncertainty on the interaction coefficient 359 of C with Fe or Sn could produce differences in the γ_{SnO2} values. The experiments of Righter et 360 al. (2017) with an MgO container yield values that are closer to those of Gortais et al. (1994) 361 362 and we have used these values to calculate the volatility of Sn (see below). Based on these 363 values of the activity coefficient for SnO₂, we obtained a regression line as a function of 364 temperature (Figure 2). For a given chemical composition, temperature is the most important source of variation of the Sn activity coefficient. 365

- 366

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

We were able to obtain a set of activity coefficients, based on the above compilation of 369 370 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.

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

377

$$Ln(\gamma_i) = \frac{A}{T} + B \qquad (10)$$

- 379
- 380

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

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

Sn	SnO ₂	1773-2173	Righter et al. (2017)
Sb	SbO _{1.5}	1873	Norris (2016)
Те	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	Те	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

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

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

397

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

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_jX_k) and quadratic terms such as X_j^2 .

401

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

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 produced simplistic thermodynamic simulations. As an initial experiment, we consider no 406 solubility of In, Sn, Sb, Te and I in the silicate melt. In this case, the condensation of these 407 408 elements is implicitly controlled by the condensation of pure compounds, i.e. indium oxide (In₂O₃), cassiterite (SnO₂), cervantite (SbO), tellurite (Te₂O₃), and lautarite Ca(IO₃)₂ (this species 409 410 is the first to be saturated among all other species present in the database). Their vapor pressures were calculated at a pressure of 50 bars for a basaltic composition and their 411 412 condensation curves are shown in Figure 3. The condensation temperatures for In, Sn, Sb, Te and I are given in Table 5. Second, one can also assume that each of these elements can form 413 414 an ideal mixture with the silicate melt assuming that the activity coefficients are equal to 1 (Henry activity coefficient for infinite dilution). The resulting condensation curves are depicted 415 416 in Figure 4, also at a pressure of 50 bars for a basaltic composition. They are significantly offset compared with the previous calculations (Fig. 3). The condensation temperatures for In, Sn, 417 Sb, Te and I are given in Table 5. These results show that assuming ideal dissolution in a silicate 418 419 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 corresponding condensation temperatures are given in Table 5. The condensation curves 427 428 calculated at four discrete pressures (1-10-50-100 bar) are shown in Figures 5 and 6 for the basalt and granodiorite compositions given in Table 2. The calculations were carried up to a 429 temperature of 4500 K. For the pressures above 50-100 bars, the initial fraction in the vapor 430 phase is in some cases slightly below one, indicating that the condensation has started at a 431 432 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 fractionation due to the half-lives of the considered elements (Plompen et al., 2020). It should 434 be mentioned here that the calculation of activity coefficients was not extrapolated beyond 435

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 (Ca(IO₃)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

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

The condensation temperatures are distinct from the boiling temperature of pure compounds 450 451 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

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

Rock composition and pressure	In	Sn	Sb	Те	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

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

The activity coefficients used in this study were derived from experimental studies and extrapolated to the relevant temperatures or chemical compositions, when available. These calculations could be improved by experimental measurements of activities for a range of temperatures and for the actual chemical compositions of the magma found after underground nuclear explosions. These activity measurements could be made thanks to a Knudsen Effusion Mass Spectrometer, as illustrated in Costa et al. (2017) who studied the 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 by physical chemists. Thus, the main parameters that control the kinetics of condensation are 479 known (e.g., Hirth and Pound 1963; Mutaftschiev 2001). First, the initial step for starting 480 condensation is to start the nucleation of a droplet or a crystal and this requires that the 481 482 system must overcome the so-called nucleation barrier which represents the minimum energy to nucleate. This energy barrier depends on the level of oversaturation, i.e. the pressure of 483 484 the species that condensate relatively to the equilibrium pressure or vapor pressure. It is well known that the greater the overpressure, the smaller this energy barrier. Second, the 485 486 nucleation is considerably eased up by the presence of a substrate. The substrate could consist of the host rock or of aerosols that may form in the vapor phase. In this case, the energy 487

488 barrier for nucleation can be lowered by a factor that depends on the wettability of the489 condensing liquid onto the substrate.

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

493
$$\frac{dn_i}{dt} = \frac{\gamma_i P_i}{\sqrt{2\pi m_i RT}} \left(1 - \frac{P_{i,sat}}{P_i}\right)$$
(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 be significantly lower than what is predicted with the common assumption of a γ_i value equal 499 500 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

As stated above, our calculations were done for a closed system evolving in chemical equilibrium at fixed pressure with a fixed amount of volatile species such as water. Real systems could exhibit additional complexities, which could produce significant deviations compared with what was calculated here. These potential complications are briefly reviewed 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 (1970), there is a rapid cooling of the overheated vapor until thermal equilibration is reached. 512 Another issue that is particularly relevant regarding the more volatile elements among those 513 514 studied here is that the vapor could cool by radiative heat loss or adiabatic expansion into fractured rocks outside the cavity. In this case, the system that we study should not consist of 515 516 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 case. To further consider the effect of vapor isolation, we have calculated in the case of the 522 523 basaltic composition at 50 bars, the condensation temperatures of In, Sn, Sb and Te from an isolated vapor produced at 3500 K. The results are plotted in Figure 8b and show that there 524 525 can be a significant shift in the condensation temperature corresponding to this situation. This calculation illustrates that it is possible to take into account such a complication, provided a 526 527 reasonable scenario is considered.

The heating of the cavity walls can lead to the vaporization of water that can then mixed with 528 529 the existing vapor inside the cavity (e.g. Chapin 1970). In this case, the water content of the initial vapor could exceed the bulk composition of the rock (i.e. basalt or granodiorite in our 530 531 cases). In order to consider the effect of this excess water on the condensation temperatures, we have calculated the condensation temperature by increasing by a factor of 2 and a factor 532 of 10 the amount of water contained in the basaltic composition (Table 2). The results 533 534 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.

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

544

545 9. Implications of condensation on radioxenon

As temperature and pressure are decreasing in the nuclear cavity, the condensation of In, Sn, Sb, Te and I, the successive precursors to radioxenon, has a direct consequence on the final accumulation of radioxenon, since the cooling rate can be fast relative to the escape rate of xenon. For a quantitative estimate of these effects, one would need a precise knowledge of 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.

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

The situation is different for the Sn isotopes ¹³¹Sn, ¹³³Sn and ¹³⁵Sn, with half-lives of 56 s, 1.45 565 s and 520 ms, respectively. In this case, there could be an effect on ¹³¹Sn with the consequence 566 that there would be a smaller in-growth of ¹³¹Xe due to partial condensation before decay 567 568 (this effect could be enhanced by the large temperature interval for Sn condensation, e.g. Figure 6). Similarly to In isotopes, ¹³⁵Sn would rapidly decay before condensation could take 569 570 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 ¹³¹Te (25 min) combined with a condensation temperature of 2040 K at 50 bars suggests that over that timescale both the temperature and 574 pressure in the cavity should have dropped significantly (e.g. Chapin 1970) to a level where 575 condensation of Te would compete with its decay. 576

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.

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

594

595 **10. Conclusions**

This study highlights that thermodynamic modeling is essential for a proper evaluation of the 596 effect of condensation of In, Sn, Sb, Te and I in a nuclear cavity following an underground 597 598 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.

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

In addition, as condensation varies with temperature, pressure and the bulk chemical composition of the system, a heterogeneous spatial distribution of the condensed radionuclides is expected in the nuclear cavity, notably among the variety of the melts produced over time (e.g., Boardman et al., 1964, Schwartz et al., 1984). This could have a strong impact on the nature and quantity of the radionuclides available for migration, particularly when estimating the hydrologic source term (e.g., Tompson et al., 2011).

Thanks to our determinations of condensation temperatures and vapor pressure in relevant conditions, it should be possible to give better estimates of the fluxes of the precursor isotopes to radioactive xenon potentially emitted from nuclear explosions as a function of the pressure and temperature of the system. As mentioned above, the dynamics of cavity formation and evolution may complicate the simple picture of a closed system condensation. Nevertheless, our work provides more realistic parameters that can be used to extend earlier studies based on pure substances, allowing better modeling of these complex systems.

628

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639 Figure captions

Figure 1 Radioactive decay chains for the 131, 133, and 135 isobars leading to xenon. 640 Horizontal arrows denote isomeric transitions, with the superscript m for the metastable 641 nuclide; other arrows denote β^{-} decay. Numbers on arrows indicate the half-lives with the 642 643 following units: second (s), minute (min), hours (hr) days (d), millions of year (Myr). Data are 644 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, 645 as well as the daughter products of xenon (Cs and Ba) as their trapping in the magma has no 646 647 effect on the Xe inventory.

648

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

651

Figure 3 Condensation curves for a basaltic composition at 50 bar, volatility controlled by the pure substances, TeO₂, SnO₂, In₂O₃, SbO₂, Ca(IO₃)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.

656

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 $Ca(IO_3)_2$ and the silicate melt ($\gamma_{MxOy} = 1$).

659

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.

662

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.

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

669

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

675

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

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