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1 **Early Diagenesis at and below Vera Rubin ridge, Gale crater, Mars**

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19 **Abstract**

20 Data returned by NASA's Mars Science Laboratory *Curiosity* rover showed evidence for
21 abundant secondary materials, including Fe-oxides, phyllosilicates, and an amorphous
22 component on and below Vera Rubin ridge in the Murray formation. We have used equilibrium
23 thermochemical modeling to test the hypothesis that these altered sediments were deposited
24 predominantly as detrital igneous grains and subsequently underwent diagenetic alteration.
25 Chemical compositions of the altered components were calculated using data returned by the
26 Chemistry and Mineralogy X-ray diffraction instrument and the Alpha Particle X-ray
27 Spectrometer on board *Curiosity*. Reaction of these alteration compositions with a CO₂-poor and
28 oxidizing dilute aqueous solution was modeled at 25 – 100 °C, with varying amounts of
29 Fe³⁺/Fe_{tot} of the host rock. The modeled alteration assemblages contained abundant
30 phyllosilicates and Fe-oxides at >100 water to rock ratios, and were directly comparable to the
31 abundances of hematite and clay minerals observed by *Curiosity* at 10,000 water to rock at 50 –
32 100 °C with pH ranging from 7.9 to 9.3. Our modeling results suggest that the hematite-clay
33 mineral assemblage is primarily the result of enhanced groundwater flow compared to the
34 Sheepbed mudstone in the Bradbury Group observed at Yellowknife Bay, and underwent further,
35 localized alteration to produce the mineralogy observed by *Curiosity*.

36 1. Introduction

37 At Gale crater, a succession of lakebed sediments has been found in the Murray
38 formation by the NASA Mars Science Laboratory (MSL) *Curiosity* rover (e.g., Grotzinger et al.,
39 2015; Edgar et al., 2020, see Fraeman et al., 2020 for an overview of the entire geologic context).
40 In this study we use thermochemical modeling to test the hypothesis that the sediments were
41 deposited predominantly as detrital igneous grains followed by diagenetic alteration conditions
42 where groundwater interacted with the sediments. This is in continuation of previous work at the
43 first units encountered by *Curiosity* at Yellowknife Bay (Bridges et al., 2015b; Schwenzer et al.,
44 2016). In doing so, we aim to constrain associated temperature, water to rock ratios, pH, and
45 redox conditions of the early diagenetic alteration that resulted in the predominantly hematite-
46 clay mineral assemblage observed in the Murray formation on and below Vera Rubin Ridge
47 (VRR). We assume that vein formation as described in L'Haridon et al. (2020) and acidic
48 alteration (Rampe et al., 2020b) belong to a later phase of alteration as well as Ca-sulfate
49 formation, which has been shown to occur during a later step of fluid evolution (Schwenzer et
50 al., 2016). The former is consistent with the sedimentological observations (Edgar et al., 2020)
51 and observations by *Curiosity's* instruments (see, e.g., McAdam et al., 2020).

52 1.1 Overview of the Murray formation

53 The Murray formation was first encountered on sol 792 of the NASA MSL mission and
54 constitutes the sedimentary units analyzed by the *Curiosity* rover from the foothills of Mount
55 Sharp (Grotzinger et al., 2015). From orbit, the lower Murray formation has areas with orbital
56 spectral signatures consistent with Fe/Mg clay, hydrated silica, iron oxides, and sulfate
57 (Anderson and Bell, 2010; Milliken et al., 2010; Thomson et al., 2011; Fraeman et al., 2013;
58 Fraeman et al., 2016). At the time of writing, the Murray formation is estimated to be ~300 m
59 thick and has been subdivided into seven members that are separated by conformable contacts, as
60 illustrated by Edgar et al. (2020). Briefly, the seven members are the Pahrup Hills, Hartman's
61 Valley, Karasburg, Sutton Island, Blunts Point, Pettegrove Point and Jura, comprised of sand- silt
62 and mudstones of lake bed and fluvial origin (Grotzinger et al., 2015; Bristow et al., 2018; Edgar
63 et al., 2018; Fedo et al., 2018; Gwizd et al., 2018; Rivera-Hernandez et al., 2019; Stack et al.,
64 2019; Edgar et al., 2020).

65 1.1.1 Stratigraphic members below Vera Rubin Ridge

66 Stratigraphic members below VRR of interest in this study were the Hartmann's Valley,
67 Karasburg, Sutton Island, and Blunts Point members (Figure 1).

68 The Hartmann's Valley member (25 m thick) has grains ranging in size between silt to
69 medium sand and with meter-scale, trough cross-bedding indicative of either fluvial or aeolian
70 settings (Bristow et al., 2018; Fedo et al., 2018; Gwizd et al., 2018). The Oudam sample was
71 drilled from this member, in fine-grained bedrock containing diagenetic Ca-sulfate mineral veins
72 (Bristow et al., 2018).

73 The Karasburg member (37 m thick) in the Murray Buttes locality is characterized by a
74 heterolithic mudstone/fine sandstone assemblage with abundant cm-scale concretions and a
75 purple hue (Fedo et al., 2018). In this member, the samples Marimba and Quela were drilled
76 from flat mudstone bedrock containing some small Ca-sulfate mineral veins and mm-scale
77 concretions (Bristow et al., 2018; L'Haridon et al., 2018; Meslin et al., 2018).

78 The Sutton Island member (98 m thick), also contains a heterolithic mudstone/sandstone
79 assemblage that is largely red in color and has an increased abundance of Ca-sulfate features
80 (e.g., veins and lenticular crystals) and polygonal cracks interpreted to result from desiccation at
81 the lake margins (Stein et al., 2018). The Sebina sample was drilled from flat, fine-grained
82 bedrock that has abundant, cm-scale nodules and Ca-sulfate mineral veins.

83 The Blunts Point member (~100 m thick) is exposed immediately below VRR on the
84 north-facing side and shares a conformable boundary with the ridge (Edgar et al., 2020; Fedo et
85 al., 2018). The Blunts Point member is characterized by well laminated mudstone with cross-
86 cutting curvilinear Ca-sulfate veins (Edgar et al., 2020). The Duluth drill sample was acquired
87 near the base of VRR in a well laminated bedrock with diagenetic raised ridges and Ca-sulfate
88 veins (Figure 1).

89 1.1.2 Stratigraphic members on Vera Rubin Ridge

90 VRR is a ~200 m wide ~6.5 km long northeast-southwest resistant geomorphological
91 feature on the northern slopes of Mount Sharp (Figure 2). VRR is composed of the Pettegrove
92 Point member that is overlain by the Jura member (Figure 1). They have a combined
93 stratigraphic thickness of approximately 60 m and were investigated by *Curiosity* from sol 1809
94 to sol 2302, when *Curiosity* traversed off VRR. The lithology at VRR appears consistent with the
95 Murray formation mudstones analyzed previously (Fedo et al., 2018; Heydari et al., 2018), with
96 a grain size similarly dominated by mud and contains occasional intervals of fine to medium
97 sandstone (Edgar et al., 2020; Rivera-Hernandez et al., 2019). APXS and ChemCam analyses in
98 the Murray formation members below and on VRR indicate that it is compositionally continuous
99 with the Murray formation, and that Fe concentrations are not elevated for VRR; this suggests
100 the compositional trends from the rocks below and the rocks on VRR are largely the result of
101 post-depositional processes, such as diagenesis (Thompson et al., 2020; Frydenvang et al., 2020).

102 Rocks within the Pettegrove Point member of the ridge are thin planar laminated, fine-
103 grained mudstones. Rocks within the Jura member at the top of the VRR stratigraphic succession
104 are also characterized by fine-grained and planar laminated facies, but with a greater degree of
105 variability in color (red, purple, grey and tan) and meter-scale inclined strata (Edgar et al., 2018,
106 2020). Generally, rocks within the Pettegrove Point member have fewer diagenetic features such
107 as nodules, mineral veins, fractures and erosion resistant features (L'Haridon et al., 2020), and
108 are lower in Al₂O₃, SiO₂, and higher in FeO_T than the Jura member (Thompson et al., 2020).
109 Both members are generally red/purple (Bennett et al., 2018) though grey bedrock patches up to
110 ~10 m in diameter have also been detected along VRR but are more common in the Jura member
111 (Frydenvang et al., 2020; L'Haridon et al., 2020). These grey patches are currently interpreted as
112 resulting from diagenesis, possibly from the circulation of warm, oxidizing, fluids (e.g., Bibi et
113 al., 2011; Peretyazhko et al., 2016, 2018; McAdam et al., 2020; Fraeman et al., 2020; Rampe et
114 al., 2020b) or reducing groundwater (Frydenvang et al., 2020; Horgan et al., 2020; L'Haridon et
115 al., 2020).

116 Three drill samples have been successfully delivered to CheMin from VRR. The Stoer
117 drill hole sampled red bedrock in the Pettegrove Point member containing some very small scale
118 (~1 mm in diameter) concretions and has the highest abundance of hematite in any sample so far
119 analyzed by *Curiosity*. The drilled samples 'Highfield' and 'Rock Hall' were acquired in the Jura
120 member in Grey and Red Jura respectively. The Grey Jura 'Highfield' sample was drilled at the
121 Lake Orcadie locality, which is within a diagenetic grey patch with abundant Ca-sulfate veins,

122 Fe-rich nodules and dark, elongate diagenetic features. MAHLI images before and after drilling
123 showed that Highfield had potentially sampled these features. The Highfield sample is also
124 notable for the likely presence of ‘grey hematite’ i.e. relatively coarse hematite with crystallites
125 $>5 \mu\text{m}$ in diameter (Rampe et al., 2020b). On the basis of Catling and Moore’s (2003) study of
126 grey hematite, Rampe et al. (2020b) inferred a lower temperature limit of $\sim 100^\circ\text{C}$ for the grey
127 hematite-bearing assemblage. The Rock Hall Jura sample was acquired just south of the grey
128 Lake Orcadie area in a red patch of bedrock with an unusual, shiny, nodular appearance.

129 1.1.3 Mineralogy of the Murray formation

130 CheMin analyzed drilled rock powders from the Murray samples Confidence Hills,
131 Mojave2, Telegraph Peak, Buckskin, Oudam, Marimba, Quela, Sebina, and Duluth below VRR,
132 and Stoer, Highfield, and Rock Hall on VRR itself (for details on the methodology see Rampe et
133 al., 2020a). Of these drilled rock powders, the last eight (Oudam through Rock Hall) belong to
134 the hematite-clay mineral group investigated in this paper. CheMin data analyses show the
135 presence of both detrital igneous minerals and products of aqueous alteration in these eight
136 drilled rock powders. Details on the mineralogy of these samples are reported by Bristow et al.
137 (2018), Rampe et al. (2020a), Achilles et al. (2020), and Rampe et al. (2020b). All eight samples
138 contain abundant primary magmatic minerals in the form of plagioclase feldspar (19 – 24 wt.%
139 of the bulk sample) with unit-cell parameters consistent with an andesine composition and lesser
140 amounts of pyroxene (1 – 9 wt.% of the bulk sample), alkali feldspar (<3 wt.% of the bulk
141 sample) and quartz (<1 wt.% of the bulk sample). The low angular resolution of the CheMin
142 instrument prevents a confident identification of the type(s) of pyroxene present (Rampe et al.
143 2020b).

144 Phyllosilicates are present in every sample but vary in structure and abundance through
145 the stratigraphy. Ferripyrophyllite ($\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), a member of the talc-pyrophyllite group, is
146 the most likely phyllosilicate in Oudam (3 ± 1 wt.% of the bulk), based on position and breadth
147 of the low intensity (001) basal peak (9.6 \AA in CheMin data) and the H_2O evolution profile
148 observed from the Oudam SAM EGA analysis (Bristow et al., 2018; Achilles et al., 2020). In
149 Marimba, Quela, and Sebina the phyllosilicate basal spacings and the positions of the (02l) band
150 suggest a mix of dioctahedral and trioctahedral smectite (e.g., Bristow et al., 2018). Smectite
151 composes 28 ± 3 wt.% of the bulk of Marimba, and the (02l) peak position is consistent with a
152 1:2 dioctahedral:trioctahedral weight abundance ratio, with SAM EGA data consistent with Fe-
153 montmorillonite and Mg-saponite (Bristow et al., 2018; Achilles et al., 2020).
154 Dioctahedral:trioctahedral ratios for the 16 ± 2 wt.% smectite in Quela and the 19 ± 2 wt.%
155 smectite in Sebina are 1:1 and 5:3, respectively, based on CheMin data (Bristow et al., 2018;
156 Achilles et al., 2020). Data from Duluth indicate the presence of exclusively dioctahedral
157 smectite. Analysis of CheMin data for Duluth indicates 15 ± 7 wt.% bulk Fe^{3+} clay, with both
158 CheMin (Rampe et al., 2020b) and SAM EGA data (McAdam et al., 2020) consistent with the
159 presence of nontronite. The basal spacings in the patterns from Stoer, Highfield, and Rock Hall
160 are at 9.6 \AA instead of the 10 \AA position attributed to collapsed smectite in previous samples
161 (Bristow et al., 2018), indicating the presence of a collapsed smectite with a small interlayer
162 cation or the trioctahedral phyllosilicate ferripyrophyllite (Bristow et al., 2018; Rampe et al.,
163 2020b). Phyllosilicate abundances for Stoer, Highfield and Rock Hall were reported to be 10 ± 5 ,
164 5 ± 2 and 13 ± 6 wt.% bulk, respectively (Rampe et al., 2020b). Overall, the abundance and
165 nature of the clay minerals in conjunction with primary magmatic minerals, allows for testing the

166 hypothesis that all or a significant proportion of the clay minerals were formed in situ during
167 post-depositional diagenesis.

168 Each drill sample contains abundant Fe-oxides and/or Fe-oxyhydroxides (Achilles et al.,
169 2020; Rampe et al., 2020b). Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is present in every sample in abundances of ~3
170 wt.% of the bulk sample for Rock Hall up to ~16 wt.% of the bulk sample for Stoer. The colors
171 of the drill tailings in Oudam and Highfield suggest grey or specular hematite is present in these
172 samples. Akaganeite ($\alpha\text{-Fe}^{3+}\text{O}(\text{OH},\text{Cl})$) is more abundant than hematite in Rock Hall, and
173 constitutes 6 wt.% of the bulk sample. A trace amount of akaganeite is present in Stoer.
174 Magnetite is present in Duluth, Stoer, Highfield, and Rock Hall near the detection limit of
175 CheMin (Rampe et al., 2020b).

176 Ca-sulfate minerals are prevalent in every sample, but vary in type and abundance
177 between samples. Most samples have all three varieties of Ca-sulfate (anhydrite – CaSO_4 ,
178 bassanite – $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$, and gypsum – $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), with the exception of Rock Hall. Rock
179 Hall has the greatest abundance of Ca-sulfate of these samples, in which ~11 wt.% of the bulk
180 sample is comprised of anhydrite. Duluth has the lowest abundance of Ca-sulfate of these
181 samples, with ~1.5 wt.% anhydrite, ~3.5 wt.% bassanite, and gypsum is at the CheMin detection
182 limit. Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) is present in abundances up to a few wt.% in Marimba, Quela,
183 Sebina, Stoer, and Rock Hall (Achilles et al., 2020; Rampe et al., 2020b).

184 All samples contain abundant X-ray amorphous materials, and FULLPAT analyses
185 indicate that opal-CT comprises a portion of the X-ray amorphous materials in the Oudam and
186 Highfield samples. Based on mass balance calculations using CheMin mineral abundances,
187 crystal chemistry using CheMin mineral abundances, crystal chemistry, and bulk APXS
188 measurements, the composition of the X-ray amorphous component is variably enriched in Si,
189 Fe, and S in these samples (Achilles et al., 2020; Rampe et al., 2020b).

190 Several hypotheses exist for the variations in mudstone mineralogy such as variations in
191 redox within the lake during the deposition of the Murray sediments (Hurowitz et al., 2017), a
192 combined effect of source composition, mineral transportation and alteration (Bedford et al.,
193 2019), diagenetic alteration at cold to low-T hydrothermal temperatures (Achilles et al., 2020;
194 Frydenvang et al., 2020; McAdam et al., 2020; Thompson et al., 2020; Fraeman et al., 2013,
195 2016; Rampe et al. 2017), or aqueous alteration of deposited sediments by a short-lived, acidic
196 fluid during late diagenesis (Rampe et al., 2017).

197 **2. Methods**

198 Thermochemical modeling is a useful tool to disentangle reaction pathways in
199 environments where a fluid has interacted with a rock and changed its initial mineralogy,
200 especially for martian environments where observations are limited compared to more accessible
201 environments on Earth. On Mars, a wide range of reaction pathway problems have been studied
202 successfully using a variety of thermochemical tools. On the basis of Martian meteorite and
203 orbital data, problems such as carbonate and acidic reactions, silicate deposition, and organic
204 molecule reactions have been studied and tested successfully against experimental or
205 observational results (Griffith & Shock, 1995, 1997; Hausrath et al., 2018; McAdam et al., 2008;
206 Tosca et al., 2004, 2008; Varnes et al., 2003; Zolotov and Mironenko, 2007, 2016; Zolotov and
207 Shock, 1999, 2005). CHIM-XPT and its predecessor CHILLER have been used to study a wide
208 range of Martian P-T regimes, mainly for clay forming environments (Bridges and Schwenzer,

209 2012; Filiberto and Schwenzer, 2013; Schwenzer and Kring, 2009, 2013; Schwenzer et al.,
210 2012), and also successfully tested against observational ground truth in meteorites (Bridges and
211 Schwenzer, 2012; Melwani-Daswani et al., 2016) and in situ on Mars (Bridges et al., 2015b;
212 Schwenzer et al., 2016; Schieber et al., 2017). It is on this basis that CHIM-XPT was used to
213 develop and test the models presented here.

214 Thermochemical modeling does, however, have limitations where extrapolation of
215 pressure-temperature thermochemical data increases uncertainty, or kinetics changes the
216 outcome of a reaction pathway compared to prediction made solely on Gibbs free energy
217 calculations. For details on this background, we refer readers to a wide range of literature (e.g.,
218 Ganguly, 2008; Holland and Powell, 1998; Kühn, 2004; Reed, 1997; Rimstidt, 2014), which will
219 provide the theoretical backing of the technique and further insights into problem solving and
220 decision making to limit the impact of the tool's limitations. It is noted that clay minerals pose a
221 problem in modeling iron-bearing environments on Mars (Catalano, 2013; Chevrier et al., 2007).
222 Therefore, in this paper, care was taken to use all information available to constrain the modeling
223 parameters when evaluating the results. It is important to note that in a sedimentary environment,
224 or any dynamic geologic environment, the models describe reaction pathways of local
225 equilibrium and not an overall equilibrium of the entire geologic unit (Kühn, 2004; especially
226 chapter 3 and the critical discussion on p. 79f. for a more detailed discussion of the problem).
227 Thus, such models enable the assessment of a reaction pathway for a given overall chemistry to
228 reach the resulting alteration assemblage.

229 2.1 Thermochemical code and database

230 CHIM-XPT (Reed et al., 2010) is a program for computing multicomponent
231 heterogeneous chemical equilibria in aqueous-mineral-gas systems and was chosen because of its
232 heritage in modeling basaltic and ultramafic systems (e.g., Reed, 1983; Palandri and Reed,
233 2004), and modeling alteration on Mars (Schwenzer and Kring, 2009; Bridges and Schwenzer,
234 2012; Schwenzer et al., 2012; Filiberto and Schwenzer, 2013; Bridges et al., 2015b; Schwenzer
235 et al., 2016; Melwani-Daswani et al., 2016; Schieber et al., 2017). Every calculation step
236 calculates equilibrium between the fluid and the dissolved rock, meaning that each step can be
237 treated and interpreted independently to the direction from which it was reached, and each step
238 determines the properties of the minimum Gibbs free energy of the system. Step size may vary
239 depending on task requirements. A weight ratio of the total number of fluid grams relative to the
240 total number of grams of reactant rock is used, so model calculations are independent of the size
241 of the system, but the calculations are usually based on 1 kg (55.5 mol) of water. Precipitates are
242 not fractionated from the system unless stated otherwise. In CHIM-XPT, the water to rock ratio
243 (W/R) is the ratio of incoming fluid to reacted host rock. Inputs required for the execution of
244 CHIM-XPT in this study were the starting fluid composition, reactant rock chemical
245 composition, system temperature and pressure. We did not include a gas phase at the start of the
246 calculations and did not replenish any CO₂ or other components typically found in the Martian
247 atmosphere. Thus, our system was closed to the atmosphere, as could be expected from a
248 subsurface fluid. We note, that gas phases were allowed to form, should they have become
249 stable, but none were observed at the conditions that led to clay and hematite formation.

250 The SOLTHERM thermodynamic database used with CHIM-XPT in this study contains
251 the following sheet silicates: talc (Mg, Fe, Mg-Al endmembers); pyrophyllite; chlorites
252 (clinochlore, daphnite, Mn-chlorite, Al-free chlorite); kaolinite; illite; montmorillonite (Ca, K,

253 Mg, Na endmembers); beidellite (Ca, H, K, Mg, Na endmembers); nontronite (Ca-, H-, K-, Mg-,
254 Na-nontronite); serpentine (antigorite, chrysotile, greenalite); sepiolite. The only member of the
255 kaolinite group the database contains is kaolinite. There is no saponite, vermiculite, or hectorite
256 in the database. Results are plotted in mineral abundance (wt.%) vs W/R, with chlorite
257 endmembers (Fe^{2+} clay mineral) and nontronite endmembers (Fe^{3+} clay mineral) combined.
258 Given the thermodynamic database is limited with regards to the full range of possible
259 phyllosilicates, in this study the modeled phyllosilicate assemblages are summed to calculate an
260 average clay mineral with average composition that is then taken as a chemical analogue to the
261 clay minerals observed in Gale crater. This is consistent with previous approaches by Bridges et
262 al. (2015b) and Schwenzer et al. (2016).

263 Critical evaluation of the results and comparison to terrestrial mineralogy are required to
264 further evaluate the modeling results. Especially at lower temperature, extrapolation of the
265 thermodynamic data from higher temperature might occur, which can lead to the occurrence of
266 mineral phases not known to form at the given pressure-temperature range. This problem is dealt
267 with through careful evaluation of every phase forming and exclusion of those known to not
268 form in the given pressure-temperature range, owing to kinetic constraints at low temperature
269 (Melwani-Daswani et al., 2016, supporting material). The temperature transition between the Fe-
270 oxides, goethite and hematite, was taken into consideration for the modeling. As documented by
271 Cornell and Schwertmann (2006; *and references therein*) fine grained goethite is stable ≤ 25 °C,
272 relative to coarse grained hematite. However, in laboratory environments where ferrihydrite was
273 stored as aqueous suspensions at 24 °C and pH between 2.5 and 12, both hematite and goethite
274 form, with maximum hematite forming between pH 7 and 8 and maximum goethite forming at
275 pH 4 and pH 12 (Schwertmann and Murad, 1983). It is noted that the formation of other Fe-
276 oxides such as ferrihydrite, goethite and akaganeite may have occurred first in the sediments of
277 Gale crater and later transformed to hematite via mechanisms documented by Cornell and
278 Schwertmann (2006; *and references therein*). However, while those precursors could have been
279 a factor in some of the rocks we are studying, such as those that had high amounts of Fe in their
280 amorphous components, it is difficult to definitively identify poorly ordered/amorphous Fe
281 phases such as ferrihydrite with *Curiosity's* payload, and at the time of writing there is no direct
282 evidence for ferrihydrite. For the purposes of this modeling study we assume direct precipitation
283 of goethite or hematite from the modeled porewater-rock interactions, and not from the alteration
284 of ferrihydrite. Magnetite was allowed to form but did not under the conditions modeled here at
285 the W/R assumed relevant.

286 A list of the minerals excluded in each model can be found in the supplementary material
287 (Table S3). It should be noted that the model calculations show finer details than any of the
288 sources of information from Mars: detection limit for CheMin on *Curiosity* is ~1 wt.% (Blake et
289 al., 2012) and the pixel footprint of CRISM is nominally 18 m, (Murchie et al., 2007) limiting
290 the detection of trace phases in both instances. Therefore, small contributions (<5 wt.%) of a
291 modeled alteration assemblage may not be directly comparable to the observed martian
292 mineralogy. Minerals modeled to form that have not been observed in the Murray formation,
293 either in-situ with *Curiosity* or remotely with CRISM, were allowed to form due to a lack of
294 justification for their removal.

295 2.2 Modeled water-rock ratio

296 CHIM-XPT thermochemically calculated mineral assemblages are illustrated in this
297 manuscript as plots of mineral abundance (weight %) vs W/R ratio. W/R ratio is a progress
298 variable where limited reactant rock dissolution occurs at high W/R with a relative increase in
299 reactant rock dissolution at low W/R. The mass of alteration minerals precipitated ranges from
300 0.01 g at 100,000 W/R to 1000 g at 1 W/R. CHIM-XPT assumes complete dissolution of the
301 defined reactant rock components in relevant W/R proportions per interaction step. While in real-
302 world systems only partial host rock dissolution occurs (making the W/R values reported here
303 comparably higher), modeling complete host rock dissolution enables a systematic investigation
304 of modeled alteration minerals and associated fluids as a function of the W/R process variable.
305 High W/R (>5,000) is representative of a system where only a small amount of the rock is
306 dissolved in a large mass of fluid (i.e., where only a limited surface area interacts with the fluid
307 and/or timescales are short). This can represent freshwater inflow environments such as in rock
308 fractures or rock surfaces exposed to regular precipitation. Lower W/R ranges are more
309 representative of little to no fresh-fluid inflow and stagnant fluids reacting with large rock
310 surfaces. Comparison to experiments and geologic analogs show that W/R of around 1000 is
311 generally comparable to water-rich diagenetic or small fracture settings, whereas lower W/R are
312 comparable to low-water diagenetic and eventually metamorphic conditions. For an in-depth
313 discussion how model and experimental water to rock ratios compare, see Olsson-Francis et al.
314 (2017). CHIM-XPT calculates the equilibrium reaction of the fluid with the precipitating phases
315 at an overall chemistry of the system.

316 3. Hypothesis and model set-up

317 The purpose of this study is to constrain the formation conditions (W/R, temperature,
318 redox, pH) under which the hematite-clay mineral assemblage observed on and below VRR
319 precipitated. More specifically, we test the hypothesis that the formation of clays and hematite in
320 the Murray formation on and below VRR stands in a continuation of previous studies that
321 assumed groundwater-type alteration. For Yellowknife Bay, the lowest point in the stratigraphy
322 encountered by *Curiosity* early in the mission, studies showed that groundwater-type,
323 circumneutral fluids could explain the clay mineral formation with sulfate formation happening
324 during a second fluid evolution step (Bridges et al., 2015b; Schwenzer et al., 2016). Hausrath et
325 al. (2018) came to a similar conclusion for Stimson formation alteration, where early olivine-
326 dominant dissolution in circumneutral fluids and no redox-change is required to explain the
327 observations. In this study, however, we focus on the alteration of a 'magmatic' host rock
328 chemistry, as could be deposited by the fluvial-lacustrine conditions described for Gale crater, in
329 a circumneutral groundwater.

330 There is a wide range of fluid-related observations and phenomena pre-VRR, such as
331 overall lake water changes (Hurowitz et al., 2017), nodules (Nachon et al., 2014) and silica-rich
332 haloes (Frydenvang et al., 2017), some of which are also observed on VRR. Other studies of
333 VRR alteration (Fraeman et al., 2020; L'Haridon et al., 2020; McAdam et al., 2020; Rampe et al.,
334 2020b; Yen et al., 2020) assume a multi-stage fluid evolution or a diversity of fluids to explain
335 their observations, which gives further support to testing the hypothesis in this paper: that the
336 first step of alteration was one of in situ diagenesis in a dilute, circumneutral fluid. This study is
337 in context of the late-stage phases (Ca-sulfate, jarosite, akaganeite) forming when fluid
338 concentrations had evolved to higher sulfate concentration, or more generally higher salinity, and

339 locally to acidic conditions (Achilles et al., 2020; L'Haridon et al., 2020; McAdam et al., 2020;
340 Rampe et al., 2020b; Yen et al., 2020). This is further supported by SAM investigations of
341 jarosite-bearing sediments showed a bimodal age distribution with a much younger potential
342 formation age for the jarosite-bearing alteration (Martin et al., 2017). Therefore, modeling the
343 reaction pathways of the late-stage Ca-sulfate, jarosite, and akaganeite is not a goal of this study.

344 3.1 The Starting Fluid

345 Gale Portage Water (GPW) (Bridges et al., 2015a, 2015b; Schwenzer et al., 2016; Turner
346 et al., 2019) was used as the fluid in this study, making results presented here for the Murray
347 formation directly comparable to the studies for Yellowknife Bay. This fluid was derived from
348 equilibrium mediation between a fluid used previously in Mars fluid-rock interaction modeling
349 (Schwenzer and Kring, 2009) and the basaltic Portage Soil composition sampled from the
350 Rocknest aeolian bedform in Gale crater (Bish et al., 2013). This assumed that Rocknest can be
351 regarded as an average crustal composition in Gale crater, and GPW is a fluid of groundwater-
352 type concentration directly derived from local bedrock. Because of the dilute nature of this fluid,
353 the chemistry of the rock reactants becomes the dominating factor in the water-rock reaction
354 modeling. Thus, providing additional confidence that reaction pathways described here are
355 directly applicable to *Curiosity's* observations in the Murray Formation. The exact W/R at which
356 the rock composition dominates the reaction is dependent on the solubility of the element
357 considered and its concentration in the rock. Influence of the fluid is highest for elements not
358 contained in the rock, which mostly concerns volatiles such as CO₂. However, CO₂ concentration
359 is low (1.68×10^{-4} mole/L) and does not typically lead to the formation of carbonates beyond
360 trace level. A detailed summary of how this fluid was derived is given in Bridges et al (2015b),
361 and the fluid composition in Table 3 of Bridges et al. (2015b). Chlorine concentrations are about
362 an order of magnitude higher, at 5.76×10^{-3} mole/L, but chlorine is not observed to participate in
363 mineral formation. It is an important carrier of ionic strength at the very highest W/R, but at the
364 W/R considered important here, does not cause any change of the system. It also is a potential
365 complexing anion to increase Fe-solubility (e.g., Cornell and Schwertmann, 2006), but Cl
366 concentrations are too low to significantly increase Fe-concentration in the fluid (Bridges et al.,
367 2015b). Our Fe-concentrations are generally in family with other similar models (e.g., Marion et
368 al., 2003). Cl-concentrations only show notable influence on apatite formation, which forms as
369 Cl-apatite instead of hydroxyl-apatite, if Cl-concentrations are significant, but forms F-apatite
370 once fluorine is present (Filiberto and Schwenzer, 2013). We note that – due to the lack of
371 quantitative fluorine data – we have not incorporated fluorine into the system. The solution is
372 initially oxidizing with all S species as SO₄²⁻, and the redox in the fluid is controlled by the SO₄²⁻
373 /HS⁻ pair. The redox of the system throughout each model is dependent on the Fe²⁺/Fe³⁺ ratio of
374 the total Fe in the reactant rock composition. The fluid composition is represented in each
375 calculated step by a set of 112 different ionic species. Unless stated otherwise, fluid pH was
376 modeled as a free parameter.

377 3.2 Host Rock Composition

378 The drill samples studied have a mixture of 'primary magmatic' phases, such as pyroxene
379 and plagioclase (Achilles et al., 2020; Rampe et al., 2020b), and alteration phases such as
380 phyllosilicates and hematite (Rampe et al., 2020b; McAdam et al., 2020). Olivine is absent in the
381 samples, which is in agreement with many literature resources that have shown it to be the first
382 mineral to dissolve (e.g., Gudbrandson et al., 2011; Hausrath et al., 2018). To model the first

383 diagenetic phase that occurred in the Murray formation, the chemistry of the observed alteration
384 must be considered. In this study, chemical alteration compositions were calculated and used as
385 the reactant host rock composition in the thermochemical modeling.

386 Calculating the chemical alteration compositions was undertaken by combining
387 measurements taken by APXS and CheMin instruments on-board the *Curiosity* rover for drilled
388 samples obtained in the Murray formation: Oudam, Marimba, Quela, Sebina, Duluth, Stoer,
389 Highfield and Rock Hall (summarized in section 1.1). Using crystal chemistries derived for the
390 magmatic minerals (Table S1) (Morrison et al., 2018; Achilles et al., 2020; Rampe et al., 2020b)
391 and their abundances determined using CheMin data (Bristow et al., 2018; Rampe et al., 2020a),
392 the associated compositional oxide wt.% contributions were subtracted from the bulk APXS
393 measurements. Ca-sulfates observed by CheMin (Achilles et al., 2020; Rampe et al., 2020b)
394 were also removed as these have been shown to have formed during late diagenesis (Nachon et
395 al., 2014), during a possible two-step process (Schwenzer et al., 2016). This approach includes
396 contributions from the amorphous component that, at the time of writing, is not well understood
397 and is hypothesized to contain primary basaltic glass, nanophase Fe-oxides, amorphous sulfates,
398 and sulfides (Bish et al., 2013; Smith et al., 2019; Rapin et al., 2019; Rampe et al., 2020a;
399 Achilles et al., 2020; Wong et al., 2020).

400 Given the young, Amazonian age inferred from K-Ar investigations of the jarosite in the
401 Mojave drill sample (Martin et al., 2017), it is also assumed that the observed akaganeite and
402 jarosite formed during late-stage acidic alteration after the formation of hematite and clay
403 minerals (e.g. Achilles et al., 2020; Rampe et al., 2020b). Thus, the formation of akaganeite and
404 jarosite is not within the scope of this study. However, their chemical composition is included in
405 the calculated alteration composition as their formation is likely the result of localized alteration
406 where elements were remobilized from the products of the first step of diagenesis that is being
407 modeled here.

408 3.3 Pressure-Temperature space

409 The temperatures selected for modeling were 25 °C, 50 °C, 75 °C and 100 °C, as this
410 broad range can be consistent with the alteration mineralogy observed in Gale crater (Bristow et
411 al., 2018; Rampe et al., 2020a). The pressure was selected to prevent boiling for each
412 temperature. Results were then evaluated with respect to temperature and used as a guide for
413 thermochemical modeling where reactant rock was the calculated chemical alteration
414 compositions for drill samples collected in the Murray formation below VRR and the overall
415 Murray formation.

416 3.4 Redox considerations

417 No direct measurements of overall redox conditions in the rock were possible (e.g.,
418 because of the presence of the amorphous phase; Achilles et al., 2020; Rampe et al., 2020b).
419 Thus, different $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of the total Fe in the host rock were modeled. Resultant mineral
420 assemblages were then compared to alteration mineral assemblages observed by *Curiosity* to
421 evaluate the accuracy of the model. Models were run at $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the host rock chemistry at
422 10% and 50% to explore the varying effect on the resultant alteration mineral assemblage. SO_3
423 was recalculated as FeS and the equivalent amount of Fe was subtracted from FeO. Cl was
424 recalculated as NaCl and the equivalent amount of Na was subtracted from Na_2O .

425 4. Model results

426 4.1 Calculation of the host rock composition

427 The result of the magmatic mineral subtraction process (section 3.2) shows a similar
428 chemical alteration composition throughout the Murray formation below VRR (Figure 3). SiO₂
429 varies between 45 and 49 wt.% (Figure 3), FeO_T has a larger variation, between 23 and 29 wt.%,
430 and a positive correlation with SiO₂. MgO varies between 5 and 7 wt.%, Al₂O₃ between 5 and 7
431 wt.%. Alkali oxides (Na₂O and K₂O) are below 2 wt.% in all calculated alteration compositions
432 below VRR. The three samples acquired on VRR display a larger variability in SiO₂, varying
433 from 35 to 54 wt.%. FeO_T has a similar variation to below VRR, varying between 23 and 29
434 wt.%. MgO is also similar in range on VRR compared to below, 3 to 6 wt.%, while Al₂O₃ is
435 lower on VRR, ranging from 3 to 6 wt.%. Alkali oxides (Na₂O and K₂O) are below 2 wt.% in all
436 calculated chemical alteration compositions on VRR.

437 For the VRR samples, there are some noteworthy observations for the chemical alteration
438 compositions (Figure 3): The Rock Hall and Highfield drill holes sampled red and grey Jura,
439 respectively, with the FeO_T in our calculation being about 5% higher in Rock Hall than in
440 Highfield. The red Jura target, Rock Hall, is very similar in FeO_T to the red Pettegrove Point
441 Stoer target. Generally, alteration assemblages high in SiO₂ appear low in FeO_T and vice versa,
442 while Al₂O₃ is lowest when FeO_T is highest. When averaged over the entirety of the drilled
443 samples, chemical alteration compositions below and on VRR are remarkably similar (Figure 4),
444 pointing towards local element mobility. This confirms our assumption of a dilute incoming
445 fluid, but also points towards the absence of a large-scale fluid movement in late-stage
446 diagenesis after the formation of the hematite-clay dominant mineral assemblage.

447 The alteration content of the different samples was also assessed, with the ratio of
448 alteration to primary mineral content detailed in Table 1. These ratios indicate that, if Ca-sulfates
449 are excluded, samples below VRR contain a greater fraction of identified alteration products
450 compared to VRR, with Duluth containing the least amount of alteration. This is consistent with
451 Mangold et al. (2019a; 2019b) who showed a decrease in the Chemical Index of Alteration above
452 the Sutton Island member. We have thus decided to model the average alteration composition of
453 VRR and compare those models to models which use an overall average alteration composition
454 and an average alteration composition for below VRR (excluding Duluth as this had further
455 diagenetic features). A comparison of the mean alteration chemical compositions for the pre-
456 VRR Murray formation (Oudam to Sebina) and for VRR Murray (Stoer to Rock Hall) shows that
457 they are similar (Figure 4, see also Table S4) with the standard deviation of these mean
458 compositions overlapping.

459 4.2 Alteration mineralogy in a groundwater-dominated setting

460 As described above, we assume that the sediments in the Murray formation on and below
461 VRR are altered in situ from 'magmatic' detrital precursors, and our model with the calculated
462 chemical alteration composition described above then allows us to compare a predicted mineral
463 assemblage with what has been observed by *Curiosity* in the Murray formation. The reasoning
464 for this is that what currently remains as unaltered pyroxene will not have taken part in the
465 reactions, and what is now the alteration assemblage was once a 'magmatic' mineral, e.g. olivine,
466 pyroxene, plagioclase, and has been reacted into the minerals we find now. Therefore, we
467 modeled four temperature steps for the average VRR Murray alteration composition. The

468 resulting mineral assemblages for all three can be divided into three W/R sections. At very high
469 W/R (above W/R of 10,000), models between 50 and 100 °C show a hematite-clay mineral
470 assemblage whereby the dominant clay is chlorite (Figures 5 and 6). At 25 °C, goethite forms
471 instead of hematite (Figures 5A and 6A). Between W/R of 10,000 and down to W/R of 100 or
472 below, nontronite dominates, and below W/R of about 100 a talc-chlorite assemblage forms. This
473 generalized pattern applies for different redox settings as well as for the VRR-only and ‘all
474 Murray’ compositions (Figures 5, 6 and 7).

475 Assessing the influence on temperature in the system that has 10% of the FeO_T as Fe^{3+}
476 (Figure 5A-D) shows that the W/R range in which nontronite forms becomes smaller and the
477 amount of nontronite forming decreases as the temperature increases from 25 °C to 100 °C.
478 Instead of nontronite, a hematite–chlorite assemblage forms at high W/R. Note also the increased
479 presence of a SiO_2 -phase with increasing temperature. At low W/R changes are more subtle,
480 leading to the formation of a few wt.% of epidote at the highest temperature. This
481 “metamorphic” assemblage is not found at Gale crater, for which reason we focus the discussion
482 in the next section on the high and intermediate W/R sections.

483 In the case of the more oxidizing system (50% of the FeO_T as Fe^{3+} ; Figure 6A-D),
484 changes are subtle. Thermochemical models run at 25 °C show goethite abundances vary from
485 7.5 wt.%, 2.0 wt.% and 0.0 wt.% for models with 10% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ to 9.6 wt.%, 1.6 wt.% and 5.2
486 wt.% for models with 50% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$, at 10,000 W/R, 1,000 W/R and 100 W/R, respectively. At
487 and above 50 °C, hematite is more thermodynamically stable than goethite and forms instead. As
488 expected, hematite content increases with increasing Fe^{3+} availability, meanwhile Fe-sulfide
489 decreases (Tables S5 and S6).

490 The nontronite field expands towards intermediate and lower W/R, and so does the SiO_2 -
491 phase, forming around W/R of 1,000 – 10,000 (Figures 5 and 6, Table S7). We note, though, that
492 the overall pattern of a hematite-clay mineral assemblage at high W/R and nontronite at
493 intermediate W/R remains stable (Table 2). However, at high W/R the dominant clays are
494 chlorites, the onset of which occurs at lower W/R with increasing temperature (Figures 5 and 6).
495 Modeling the different Murray averages (Table S4) at 50 °C and at 10% and 50% FeO_T as Fe^{3+}
496 returns almost indistinguishable results (Figure 7), which demonstrates that the hematite-clay
497 mineral assemblage is the dominant assemblage at high water to rock ratios over a wide range of
498 environmental conditions.

499 4.3 Summary of the Modeled Alteration Mineral Assemblages

500 Thermochemical modeling undertaken for this study has focused on producing the
501 hematite-clay mineral alteration assemblage observed in the Murray formation, with emphasis on
502 sedimentary rocks on and below VRR. Chemical compositions of the alteration mineral
503 assemblages observed by *Curiosity* were calculated and used as the reactant rock chemical
504 compositions for thermochemical modeling. Modeled alteration mineral assemblages have been
505 produced for a variety of W/R, temperatures and varying $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ content (Figures 5 and 6).

506 For the models in this study, at and above 50 °C hematite forms likely a result of it being
507 more thermodynamically stable than goethite (Cornell and Schwertmann, 2006 *and references*
508 *therein*) and makes these models directly comparable to observations by *Curiosity*. Table S5
509 gives details of the modeled hematite abundances showing an increase in hematite abundance
510 with temperature at 10,000 and 1,000 W/R, with an additional increase associated with Fe^{3+}

511 availability. Magnetite was allowed to form in the models (Figures 5 and 6) but did not form at
512 the W/R assumed relevant. Table S6 demonstrates that Fe-sulfide abundance increases with
513 temperature at 10,000 W/R with minor wt.% variation at 1,000 W/R and 100 W/R. Fe-sulfide
514 abundances decrease at all W/R with increased Fe³⁺ availability.

515 The dominant clay minerals, when formed in our thermochemical models belong to the
516 smectite group (nontronite), though in some cases significant chlorites form. Clay mineral
517 abundance varies significantly with temperature. In summary, the overall clay abundance
518 decreases with temperature regardless of Fe³⁺ availability (Table S8); however, there is an
519 increase in clay abundance at 1,000 W/R and 100 W/R from 10% Fe³⁺/Fe_{tot} to 50% Fe³⁺/Fe_{tot} at
520 each modeled temperature. Summed in Table S7, there is a clear decrease in nontronite
521 abundance with temperature and a significant increase at 100 W/R with increased Fe³⁺
522 availability. The chlorite abundance increases with temperature and decreases with Fe²⁺
523 availability (Table S9). The third group of clay minerals that formed in the models in this study
524 was talc; for each modeled temperature, talc forms with increasing abundance from 10,000 – 1
525 W/R (Figures 5 and 6). Overall, talc abundance decreases with temperature and Fe²⁺ availability
526 (Table S10).

527 Thermochemical modeling at 50 °C for the calculated alteration chemical compositions
528 for the rocks below VRR and the overall Murray formation (Figure 7) returned near
529 indistinguishable results at high W/R compared to the calculated chemical alteration composition
530 for the rocks on VRR (Figures 5 and 6). This implies dominance of a hematite-clay mineral
531 assemblage for high W/R over a range of environmental conditions.

532 To assess redox, all Fe- and S-bearing phases have to be taken into account. We note here
533 that ferrous (including magnetite as a Fe-oxidation state mineral) and ferric minerals form at
534 different W/R. The main influence on redox is expected from variations in the host rock
535 chemical composition, especially in a subsurface system without access to atmospheric CO₂.
536 While, as stated in the results section, the main silicate mineral composition remains largely
537 unaffected by redox, there are differences in the hematite/sulfide ratio (Figures 5 and 6). Taking
538 75 °C as an example (Tables S5 and S6), 9.6 wt.% hematite and 10 wt.% pyrite precipitate from
539 the system at 1,000 W/R and 10% Fe_{tot} as Fe³⁺. In contrast, at 50% Fe_{tot} as Fe³⁺ in the host rock,
540 the hematite/sulfide ratio increases from approximately 1 to 1.4 (12 wt.% hematite and 8.5 wt.%
541 pyrite). However, at lower temperatures, and higher and lower W/R, the situation is different.

542 The pH for the models shown in this paper (Figures 5 and 6) at 10,000 W/R ranges from
543 7.9 to 9.3, as shown in Figure 8. At 10,000 W/R for the VRR Murray composition derived in
544 Table S4, the pH trends from 9.4 to 8.0 for 25 to 100 °C at 10% Fe³⁺/Fe_{tot} content and 9.2 to 7.9
545 for 25 to 100 °C at 50% Fe³⁺/Fe_{tot} content. For pre-VRR Murray and overall Murray
546 compositions in Table S4, the pH is 8.8 for 10% Fe³⁺/Fe_{tot} content and the pH is 8.7 for 50%
547 Fe³⁺/Fe_{tot}. We attribute this increase in pH with decreasing W/R to H being consumed by
548 phyllosilicate formation as increasing pH is commonly observed with decreasing W/R and
549 increasing phyllosilicate formation (e.g., Schwenger and Kring 2009, Bridges and Schwenger,
550 2012; Bridges et al., 2015b).

551 5. Discussion

552 Our discussion first assesses the modeled mineral assemblages in context with the
553 observations of the Murray formation. We then compare to other Martian-based models before
554 looking at terrestrial comparisons.

555 5.1 Comparison of modeled mineral phases with Murray formation observations

556 The modeled early diagenetic mineral assemblages (Figures 5, 6 and 7) were compared to
557 mineral phases observed by CheMin. To compare the modeled clay minerals to observations in
558 the Murray formation, their chemistry is considered in section 5.3. Whilst the modeling method
559 used in this study calculates chemical equilibrium at specific W/R, it is important to remember
560 that low-temperature diagenetic processes are dominated by chemical kinetics (Misra, 2012). For
561 this reason, we rely on comparisons with the ground truth – the observed mineralogy at VRR –
562 for the setup of our model and the interpretation of our results. It is the combination of ground
563 truth from the rover instruments with the models that allow us to arrive at our conclusions.

564 The abundances of Fe-oxides formed in the models varies with $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ content and,
565 depending on temperature, speciation. Thermochemical models run at 25 °C do not compare well
566 with *Curiosity* observations with regards to Fe-oxide abundance with clay (Tables 2 and 4), and
567 as hematite, not goethite, is observed in the drilled samples (Achilles et al., 2020; Rampe et al.,
568 2020b). As goethite can transform to hematite over time (Cornell and Schwertmann, 2006 *and*
569 *references therein*) there is a possibility that these lower temperature models reflect the actual
570 reaction pathway, and that the hematite-clay mineral assemblage observed in the Murray
571 transformed from a goethite-clay mineral assemblage with burial and diagenesis of the
572 sediments. It is important to note that, like goethite, ferrihydrite or magnetite may have also been
573 precursors to the hematite observed in the Murray formation. This possibility is discussed by
574 Achilles et al. (2020) for the hematite observed in Oudam and Rampe et al. (2020b) for the
575 samples on VRR. The mechanisms to transform ferrihydrite to hematite include aqueous
576 suspension under weakly acidic to weakly alkaline pH, and aging in a humid environment
577 (Cornell and Schwertmann, 2006 *and references therein*). These mechanisms are discussed by
578 Rampe et al. (2020b) for VRR with particular note on hematite crystallite size being an indicator
579 for formation process. Magnetite was observed by *Curiosity* on VRR in Duluth, Stoer and
580 Highfield (Rampe et al., 2020b), and is also a potential pre-cursor that can be transformed to
581 hematite by oxidation. The magnetite chemistry was included in the chemical alteration
582 compositions. Therefore, the models do not rule out the transformation of other Fe-oxides to
583 hematite. However, in this study it is assumed that the present-day Fe-oxides observed in the
584 Murray formation and VRR are what precipitated at the time of formation and have not since
585 transformed, and so the thermochemical modeling results are compared to *Curiosity*
586 observations.

587 Trace amounts of calcite, rhodochrosite, merwinite and spurrite were not included on the
588 thermochemical model plots (Figures 5, 6 and 7). This is because the presence of phases such as
589 spurrite ($\text{Ca}_5\text{Si}_2\text{O}_8(\text{CO}_3)$) and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$) indicate a fluid rich in Ca. This is likely
590 the result of Ca-sulfate contamination, which have been observed extensively in Gale crater
591 (section 1). Trace amounts of carbonates such as calcite and rhodochrosite have not been
592 observed with CheMin in the samples in this paper at the time of writing (January 2021).
593 However, it has been indicated that siderite may be present in Rock Hall (Rampe et al., 2020b),
594 and carbonates have been identified in SAM EGA data of samples from the Stimson formation

595 encountered earlier in the mission (Sutter et al., 2017). We note that it has been suggested, using
596 an experimental approach on martian crust simulants, that carbonates only form when olivine is
597 abundant and would not form in olivine-free assemblages under a CO₂ atmosphere (Baron et al.,
598 2019).

599 The hematite/sulfide ratio is mainly controlled by the variation in the onset of nontronite
600 formation (at systematically lower W/R with increasing temperature) under high-W/R
601 conditions, and at low-W/R by the ratio of nontronite to celadonite as Fe-phyllsilicate phase.
602 This demonstrates that the main redox sensitivity of such systems might not be discernible via
603 the clay minerals alone. We note that phyllosilicates and their role in interpretation of the Mars
604 samples is still being refined (Hurowitz et al., 2017; Bristow et al., 2018) and models suffer from
605 uncertainties in the thermochemical data for these minerals (Catalano, 2013). Thus, it is
606 encouraging to see that the system changes within strictly constrained boundaries of the input
607 redox parameter conditions of the host rock.

608 5.2 Comparison of Modeled Mineral Abundances to those observed Murray Formation 609 Mineralogy

610 For comparing the modeled mineral assemblages in this paper to observations made by
611 *Curiosity*, we also considered the relative abundance of the observed altered phases. The
612 observed CheMin clay mineral / Fe-oxide ratios in Table 4 are most comparable with the
613 modeled ratios at 50 °C and 10,000 W/R shown in Tables 2 and 3, as also shown in Figure 9.
614 Figure 9 shows that the observed CheMin ratios are not comparable with modeled clay mineral /
615 Fe-oxide ratios at 50 °C for 1,000 or 100 W/R. Summing all Fe-oxides reported by CheMin
616 significantly lowers the clay mineral / Fe-oxide ratio for the VRR mean ratio (Table 4), largely
617 due to akaganeite in the Rock Hall drilled sample. As previously discussed, we note that
618 akaganeite might belong to a later alteration phase and formed independent of the hematite-clay
619 mineral diagenetic environment where Fe is remobilized. In Figure 10, CheMin abundances of
620 clay minerals and hematite are normalized to the calculated alteration component, which
621 includes the composition of the amorphous component. The corresponding clay mineral and
622 hematite abundances at 10,000 W/R from our thermochemical models at 50 °C reveal parallel
623 negative correlations with CheMin samples Marimba, Sebina, Quela, Highfield and Oudam.
624 Linear regression analysis revealed the comparability of these trends, with a gradient $-2.35 \pm$
625 0.09 for the thermochemical models run at 50 °C and -1.88 ± 0.56 for Oudam, Marimba, Sebina,
626 Quela, Duluth, Highfield and Rock Hall, with respective R² values of 0.99 and 0.70. The error
627 associated with Duluth clay mineral and hematite abundance is within this negative correlation,
628 so was included in the regression analyses. Rock Hall does not clearly align with this negative
629 correlation, so to test whether it can be considered an outlier, linear regression was performed on
630 Oudam, Marimba, Sebina, Quela, Duluth and Highfield, which revealed a gradient of $-2.56 \pm$
631 0.45 with an R² value of 0.89. The improvement of the fit confirms that Rock Hall can be
632 considered an outlier, which is further suggestive of alteration after the initial hematite-clay
633 mineral main phase alteration modeled in this paper. In Figure 10, the position of Stoer relative
634 to negative correlation of clay minerals and hematite in Marimba, Sebina, Quela, Highfield and
635 Oudam is comparable to the position of the thermochemical models run at 50 °C relative to those
636 run at higher temperature (75 °C and 100 °C). This shows a possible increase in temperature for
637 the formation of the main phase alteration mineral assemblage in Stoer.

638 The plotted data in Figure 10 also show that, although the bulk alteration composition
639 used in the thermochemical models varies to a relatively minor extent (Table S4), such small
640 variations impact the precipitated amounts of clay minerals and hematite in the thermochemical
641 model results. However, this variation in modeled mineral abundance corresponds to modeled
642 CheMin secondary mineral abundance. In Figure 10, the shift between the trend in the CheMin
643 detections and the trend in the thermochemical models raises the question of the role of the
644 CheMin amorphous component, as chemical contributions from the amorphous component
645 detected by APXS were included in the chemical alteration compositions used in the
646 thermochemical modeling.

647 Here we assume the amorphous component includes sample constituents that cannot be
648 identified from CheMin data because crystalline materials in the samples below 1 wt.% are
649 included in the amorphous component. The composition of this amorphous composition is
650 estimated using CheMin-APXS FULLPAT analysis (Rampe et al., 2020b; Achilles et al., 2020).
651 The origin of the X-ray amorphous component is presently not fully understood. However,
652 studies have indicated the presence of nanophase Fe-oxides, amorphous sulfates, silicates and
653 low amounts of basaltic glass in the amorphous component (Bish et al., 2013; Smith et al., 2019;
654 Rapin et al., 2019; Rampe et al., 2020a). A study by Bridges et al (2015b), where Portage soil
655 was used in the starting composition, assumed that the amorphous component contained volcanic
656 or impact glass, which was then reacted together with olivine to successfully model the alteration
657 assemblages observed at Yellowknife Bay. As mentioned in section 1.1, the amorphous
658 composition is high in Fe and Si, suggesting the presence of nanophase Fe-oxides and
659 amorphous silica in the sedimentary rock (Rampe et al., 2020a; Achilles et al., 2020).
660 Considering the models presented in this paper assume that all mineralogy is essentially
661 crystalline, the linear shift between modeled and observed trends in Figure 10 could be attributed
662 to an unreacted component of the calculated alteration composition in the drill samples. The
663 Marimba, Quela, Sebina, Highfield and Stoer mineral abundances are clustered close to the
664 thermochemical models run with their alteration compositions. As previously noted, the position
665 of Stoer is comparable to higher temperature (75 °C and 100 °C) thermochemical models.

666 We tested the idea that the amorphous component might only partially belong to the
667 alteration materials by removing the amorphous component from the CheMin mineral
668 abundances for each drill hole and re-normalizing. This improves the fit between
669 thermochemical model results and CheMin observations with regards to the negative correlation
670 between hematite and clay mineral abundances (Figure 11). Although there are comparable
671 negative correlations, albeit of different gradients, between the drilled samples analysed by
672 CheMin and the thermochemical models in Figure 11, the trend with temperature shown in
673 Figure 10 is lost. This suggests that a part of the amorphous component is reactive. We
674 hypothesize that the CheMin alteration composition was not fully reacted during this phase of
675 alteration. Therefore, this could suggest that the amorphous component had a reactive component
676 and a non-reactive component or that time was insufficient to fully react the amorphous
677 component. The latter could be indicative of the alteration of a volcanic glass (e.g. Wolff-
678 Boenisch et al., 2004). Considering the modeling method assumes complete host rock dissolution
679 and igneous phases are still present in *Curiosity* observations, an unreacted igneous glass
680 component is favored here.

681 5.3 Clay Minerals and Comparisons to Yellowknife Bay and other Martian terrains,
682 including the Nakhlite Martian Meteorites

683 The results of this work can be compared to earlier theoretical modeling involving
684 general Martian compositions deduced from Martian meteorite compositions (e.g., Schwenger
685 and Kring, 2009; Filiberto and Schwenger, 2013), the composition of rocks at Yellowknife Bay
686 in Gale crater (Bridges et al., 2015b; Schwenger et al., 2016), and the nakhlite Martian meteorite
687 alteration (Bridges and Schwenger, 2012). Those models are based on varying knowledge of the
688 reaction path, with general assumptions on the alteration paragenesis from orbiters for the first
689 set of models, more precise knowledge of alteration mineral occurrence from CheMin at
690 Yellowknife Bay, and finally a detailed investigation of the alteration assemblage in the nakhlite
691 meteorites. Our study is comparable to the Yellowknife Bay study (Bridges et al., 2015b) in the
692 level of knowledge of the alteration assemblage, and comparisons between the Yellowknife Bay
693 Sheepbed member of the Bradbury Group and the Murray formation are particularly important in
694 understanding the evolution of fluids in the Gale crater sediments. The dioctahedral nontronite in
695 our models is a close analogy to the dioctahedral smectite identified in Murray (Bristow et al.,
696 2018), therefore our models have identified a possible diagenetic process to form the hematite-
697 clay mineral assemblage in the Murray formation. The phyllosilicate-bearing assemblage
698 analyzed in the Gale sediments contains no serpentine, chlorite and, at most, traces of illite
699 (Bristow et al., 2018; Rampe et al., 2020b). Phyllosilicates are widespread in the Murray
700 formation and, when present, dominated by smectites.

701 We start by comparing our assemblage to general Martian alteration deduced from orbiter
702 observations and the MER rovers. The basis for these models were Martian meteorite
703 compositions, e.g., LEW88516 for the models presented by Schwenger and Kring (2009). Based
704 on this poikilitic shergottite composition, the models are dominated by forsteritic olivine (57
705 vol.%, with contributions from pyroxene (22 vol.%) and plagioclase (16 vol.%) (Gleason et al.,
706 1997). These models showed that there are two important observations: nontronite – which is
707 observed from orbit (Ehlmann et al., 2009; Miliken et al., 2010; Carter et al., 2013) and used as
708 the anchor point for this study – most frequently occurs at intermediate temperatures (~150 °C)
709 and is replaced by chlorite and eventually amphiboles at the higher temperatures of up to 350 °C.
710 At lower temperatures (<90 °C) the dominance of forsteritic olivine causes talc formation to
711 become more dominant. The system is, however, multi-dimensional, as W/R also influences the
712 assemblage, with nontronite generally dominant around W/R of 1,000, being replaced by other
713 phyllosilicates and eventually amphiboles towards lower W/R. At the highest W/R (e.g. 10,000)
714 hematite dominates, with some nontronite. The results are similar to the results of this study
715 focusing on the Murray formation of Gale crater in the comparable pattern of hematite
716 dominance at the highest W/R. They differ in the occurrence of talc at the lower temperatures,
717 which can be explained by the difference between LEW88516 and our calculated alteration
718 compositions for the Murray formation in the MgO concentration (24 wt.% for LEW88516)
719 (Schwenger and Kring, 2009) vs. 5 wt.% (Table S4). This highlights the importance of host rock
720 composition for the alteration mineral formation, along with the effect of temperature and
721 different W/R ratios. The importance of host rock composition is also highlighted by the fact that
722 models with ‘Home Plate’ MER Spirit rock ‘Fastball’ composition form nontronite at
723 temperatures as low as 13 °C (Filiberto and Schwenger, 2013). Filiberto and Schwenger (2013)
724 hypothesized that 13 °C was the temperature at 1 km depth if the surface temperature is zero and
725 the Martian geothermal gradient is 13 °C (Babeyko and Zharkov, 2000). MgO concentration in
726 the assumed host rock is 12 wt.%, significantly lower than for LEW88516, but higher than in this

727 study. MgO/Al₂O₃ ratios are 7.6 for LEW88516, 1.5 for Fastball, and 0.97 for the models in this
728 study (Table S4). This significantly influences the stability of talc compared to nontronite, but
729 also the W/R at which the transition between nontronite and chlorite occurs. Those studies
730 (Filiberto and Schwenzer, 2013) were based on well-known host rock compositions, but for the
731 Gusev alteration mineral assemblage only orbiter data could be used.

732 Previous modeling for the Sheepbed unit (Bridges et al., 2015b) was based on Portage
733 Soil with 13 wt% MgO, and an MgO/Al₂O₃ ratio of 0.92 (Blake et al., 2013). Clay minerals
734 formed in the first stage of the model, because sulfate minerals were only observed in later veins
735 (Bridges et al., 2015b; Schwenzer et al., 2016). The models showed that the secondary mineral
736 assemblage formed by the reaction of a CO₂-poor and moderately oxidizing, dilute aqueous
737 solution with the sedimentary rocks at 10–50°C and W/R of 100–1,000, pH of ~7.5–12 (but
738 mainly near neutral through most of the reaction range). Modeled phyllosilicates were Fe-
739 smectite and chlorite. The bulk phyllosilicate composition was close to saponite stoichiometry,
740 which is inferred from CheMin data (Vaniman et al., 2014) though more Fe-rich than the bulk
741 clay mineral composition predicted here for the Murray formation at high W/R (Figure 12).

742 The nakhlite meteorite alteration assemblage's reaction pathways were assessed in a
743 different way (Bridges and Schwenzer, 2012), because both the host rock and the alteration
744 assemblage are known to a high level of detail, including precipitation and re-dissolution
745 successions (e.g. Hicks et al., 2014; Bridges et al., 2019). As a consequence of that knowledge,
746 the host rock composition could be adapted to match differences in dissolution of individual
747 mineral phases. The model concentration has 9 wt.% MgO, and the MgO/Al₂O₃ ratio is 1.9.
748 Furthermore, the observations of the alteration mineral succession in the meteorites indicated a
749 two-step process, carbonate formation first, followed by the silicate-forming phase. This caused
750 a change in the fluid during mineral precipitation, with the silicate-stage fluid being enriched in
751 Si, Na, Al, and K. Taking this into account, Fe-smectites form over a wide range of W/R down to
752 100 W/R or as low as 10 W/R (Bridges and Schwenzer, 2012). This study on Martian meteorites
753 demonstrates the importance in the accuracy of reaction pathway models presented here for
754 observations on the nature of the alteration phase, as well as any indication of differences in
755 alteration conditions for different stages of alteration.

756 For the Sheepbed mudstone of the Bradbury Group there exists the same level of detailed
757 mineralogical knowledge on pre and post alteration mineralogy as we have for the VRR-Murray
758 formation rocks. CheMin X-ray diffraction patterns and SAM evolved gas analyses from
759 mudstone samples demonstrate that phyllosilicate types and abundances vary within the
760 stratigraphic section. Abundant (~20 wt.% of the bulk) Fe³⁺-bearing saponite (a trioctahedral
761 smectite) was identified in mudstone from the Yellowknife Bay formation at the base of the
762 section (Treiman et al., 2014; Vaniman et al., 2014). Mudstone from the Pahrump Hills member,
763 ~60 m up section from Yellowknife Bay and at the base of the Murray formation, has little to no
764 phyllosilicate (up to 8 wt.% of the bulk), and CheMin XRD patterns are consistent with the
765 presence of collapsed smectite (Rampe et al., 2017). Much of the Murray formation
766 stratigraphically above the Pahrump Hills member has abundant (up to 28 wt.% of the bulk)
767 collapsed smectite (Bristow et al., 2018). Both CheMin and SAM data suggest that the structure
768 of the smectite changes from being dominantly trioctahedral (i.e., saponite) lower in the section
769 to being dominantly dioctahedral (i.e., montmorillonite and/or nontronite) higher in the section
770 (Bristow et al., 2018). Duluth was the first sampled analyzed by *Curiosity* to clearly contain only
771 dioctahedral smectite (nontronite, in this case) (Rampe et al., 2020b; McAdam et al., 2020).

772 Phyllosilicates on VRR are distinctly different from those detected in mudstone stratigraphically
773 below the ridge. The abundance of phyllosilicates on VRR is relatively low compared to much of
774 the Murray formation (e.g., Highfield contains 5 wt.% phyllosilicate) (Rampe et al., 2020b).
775 Based on our models, this decrease in phyllosilicates likely relates to the aqueous alteration
776 environment being more oxidizing on the VRR relative to that below (Figure 10). Furthermore,
777 the phyllosilicates on VRR show a 9.6 Å basal spacing, rather than a 10 Å basal spacing
778 observed in nearly all other phyllosilicate-bearing XRD patterns. This suggests that the
779 phyllosilicate is either a completely collapsed smectite, possibly from alteration in acidic fluids,
780 or that the phyllosilicate is a non-expanding clay mineral, like ferripyrophyllite. SAM data are
781 also consistent with completely collapsed nontronite or ferripyrophyllite on VRR. A similar
782 phyllosilicate was observed in very low abundances in the Oudam sample, drilled
783 stratigraphically above the Pahrump Hills member (Bristow et al., 2018), and the mineralogical
784 similarities between Oudam and Highfield from the gray Jura suggest a comparable aqueous
785 alteration history, as also suggested by our model results (Figure 10). However, Bristow et al.
786 (2018) hypothesized a detrital origin for ferripyrophyllite at Oudam.

787 There is a notable similarity in trioctahedral saponite observed in Sheepbed mudstone
788 (Vaniman et al., 2014) and the phyllosilicate identified in the nakhlite martian meteorites. Some
789 of these 11 meteorites contain ferric saponite with a trioctahedral structure (Hicks et al., 2014).
790 Trioctahedral saponite as an alteration product of Martian mafic material can be regarded as one
791 of the expected types. Fe/Mg smectites, whether tri or dioctahedral have been identified in
792 numerous places from orbit by reflectance spectroscopy (e.g. Ehlmann et al., 2011; Bibring et al.,
793 2006). In the thermochemical models presented in this paper for the Murray formation, the
794 dioctahedral clay nontronite is dominant at W/R up to 10,000 (Figures 5, 6 and 7). Similar to the
795 Gale *in situ* analyses, serpentine is absent and chlorite is only dominant at extreme W/R, >10,000
796 in our models. The slightly elevated temperatures of the models in this study (50–100 °C)
797 compared to thermochemical modeling for Yellowknife Bay (10–50 °C; Bridges et al., 2015b),
798 suggests that the fluids may have been sourced from deep, warm aquifers. To further compare
799 the results of this study to previous works, we have summed the phyllosilicate chemical
800 composition for the models in this paper and included them on a ternary plot in Figure 12, with
801 comparisons to previous modelling at Yellowknife Bay (Bridges et al., 2015b) and martian
802 meteorite studies (Hicks et al., 2014). As shown in Figure 12, the modeled phyllosilicates at W/R
803 10,000 in this study are close to observed Fe-saponites from the nakhlites (Lafayette) and
804 Sheepbed unit model saponite (Bridges et al., 2015b). Murray formation modeling in this paper
805 at 1,000 and 100 W/R trend towards a nontronite composition, as shown in Figure 12.

806 5.4 Comparison to alteration processes in terrestrial environments

807 Impact-craters are long recognized as depressions in which lakes, and sediments,
808 accumulate (Cabrol and Grin, 1999; Osinski et al., 2013). Gale crater is no exception, as
809 recognized early in the MSL mission and ever since, *Curiosity* is exploring a rich stratigraphy of
810 lakebed sediments (e.g., Edgar et al., 2020; Fedo et al., 2018; Grotzinger et al., 2014, 2015;
811 Hurowitz et al., 2017; section 1). Our hypothesis is that the clay-hematite assemblage is
812 predominantly the result of the first phase of diagenetic alteration that affected the sediments
813 brought into Gale crater. The sedimentary textures within Gale crater, such as cross-bedding, and
814 coarser units such as conglomerates (Williams et al., 2013; section 1) thereby support the
815 assumption of a dynamic environment with freshwater inflow. This underpins our assumption of
816 a dilute, circumneutral 'groundwater-type' fluid as the initial pore fluid. The main difference

817 between most of those settings and terrestrial analogues is, unfortunately, one of host rock
818 composition as most of Earth's examples are in more evolved rocks and/or less iron-rich than the
819 compositionally-basaltic sequences at Gale crater.

820 Several terrestrial impact craters show sedimentary sequences of lake bed characteristics,
821 starting with coarse grained sequences gradually transitioning to finer grained sequences, but
822 with considerable variation and cyclicity, e.g., the Gardnos impact structure in Norway (Kalleeson
823 et al., 2008) and the Boltsh impact structure in the Ukraine (Gilmour et al., 2013). The $14.808 \pm$
824 0.021 Ma (Schmieder et al., 2018), 24 km diameter Ries impact Crater (Nördlingen, Germany)
825 has been compared to Gale crater (Arp et al., 2019) as it contains a succession of lake bed
826 sediments and is a closed basin. Interestingly, the transport distances for conglomerates at Ries
827 are considered to be short due to impact-pre-processing (Arp et al., 2019). The sequence begins
828 with clastic sediments with conglomerates and evidence of cyclicity including variation in
829 geochemical properties of the lake (oxygen fugacity, salinity, acidity, and new freshwater inflow;
830 Jankowski, 1977; Arp et al., 2013), which is similar to observations at Gale of fan deposit
831 formation (Williams et al., 2013) and a complex lake chemistry (Hurowitz et al., 2017). This
832 shows that sedimentation was accompanied by significant quantities of water, and therefore a
833 groundwater-type scenario as assumed in our study is plausible. Alteration mineralogy of the
834 original target rock is consistent with a low-temperature alteration process (Muttik et al., 2008),
835 whereby clays are montmorillonite-type smectites. This is comparable to our findings of
836 nontronite, as the difference in clay minerals reflects the chemical differences of the host rock:
837 gneiss fragments dominated by feldspars at Ries crater, basaltic sediments dominated by mafic
838 phases and plagioclase at Gale crater. The higher Fe-content of the rocks at Gale crater, 23-30
839 wt.% (Table S2), compared to the Ries basement rocks, 2-9 wt.% (von Engelhardt, 1997),
840 explains the different clay mineral chemistry but maintains the low-temperature, groundwater-
841 driven clay formation environmental conditions.

842 We next compare to a setting more comparable in chemistry while noting that Fe-
843 concentrations at VRR are still higher than those of most terrestrial basalts; Lonar crater
844 (Hagerty and Newsom, 2003) and the basalt alteration widely observed in the Deccan trap
845 basalts. In the Northeastern part of the Deccan Traps, near Jabalpur, unweathered basalts
846 generally contain between 11 and 15 wt.% FeO_{tot} (Peng et al., 1998). Investigation of
847 sedimentary and weathered basalt samples by Salil et al. (1997) in the same region near Jabalpur
848 show that clay minerals have a similar FeO_{tot} content compared to the basalts: between 10 and 17
849 wt.% with a dominance of Fe_2O_3 . Iron concentrations between rock and alteration assemblage
850 appear constant, if not slightly higher in the sediments and basaltic alteration assemblages, which
851 is comparable to our observations where Fe in the fluid is generally very low ($\sim 10^{-9}$) at 10,000
852 W/R (Figure S1). For the Deccan Traps, Fe-concentrations in runoff water of the region appear
853 comparably very low as they are not reported for the region (Gupta et al., 2011), or more widely
854 in cold and warm spring waters as well as runoff across the Deccan (Minissale et al., 2000).
855 Clay-mineralogy in the sediments and Deccan alteration is Fe, Mg-rich smectites, which the
856 authors describe as similar to but not quite nontronitic as the Fe-content is below 50% (Salil et
857 al., 1997). This shows that water-dominated, groundwater-rock reactions such as proposed here
858 occur in weathering or diagenetic environments and are similar to the observed clay mineralogy
859 at the Gale site and in our models.

860 6. Conclusions

861 In this paper we showed that local element mobility rather than large scale, basin-wide
862 fluid movement is the most likely alteration mechanism for the main phase of alteration in the
863 Murray formation. For this, we derived chemical alteration compositions using data from
864 CheMin (Achilles et al., 2020; Rampe et al., 2020b) and APXS (Thompson et al., 2020) and
865 found them to be very similar for the Murray formation below as well as on Vera Rubin ridge.
866 After this main phase, based on the age dating and the local nature of its occurrence, a younger
867 alteration event caused the observed akaganeite and jarosite, whereby we assume that Fe was
868 remobilized from the mineral assemblages in our models (i.e. Fe-sulfides).

869 Our thermochemical modeling results indicate that the alteration that produced the early
870 diagenetic hematite-clay mineral assemblage in the Murray formation, below and on VRR, can
871 be explained by reaction of dilute brine with the calculated alteration compositions at
872 temperatures between 50 and an upper limit of 100 °C, and at a notably high W/R of
873 approximately 10,000 with pH ranging from 7.9 to 9.3. Modeling at 25 °C produces goethite,
874 which could transition to hematite at a later stage however, this phase together with the relative
875 abundances with the clay content are not directly comparable to *Curiosity* observations. We
876 interpret the high W/R as enhanced groundwater flow through this part of the Gale sedimentary
877 sequence compared to that in the Bradbury Group and its Yellowknife Bay mudstone.

878 The trends between the modeled and observed phyllosilicate and hematite abundances are
879 comparable, but not exact due to our model not precipitating metastable phases such as the
880 CheMin amorphous component. We interpret the amorphous component to have partially
881 contributed to the phase of alteration modeled in this study. Future work is necessary to
882 determine the composition and origin of the CheMin amorphous component, and thus how its
883 chemistry can be most appropriately used in thermochemical modeling studies. We will continue
884 modeling the Gale crater sedimentary mineral assemblage which in future work we aim to extend
885 from the Bradbury and Murray-VRR, into the clay-bearing Glen Torridon and overlying Sulfate
886 Units.

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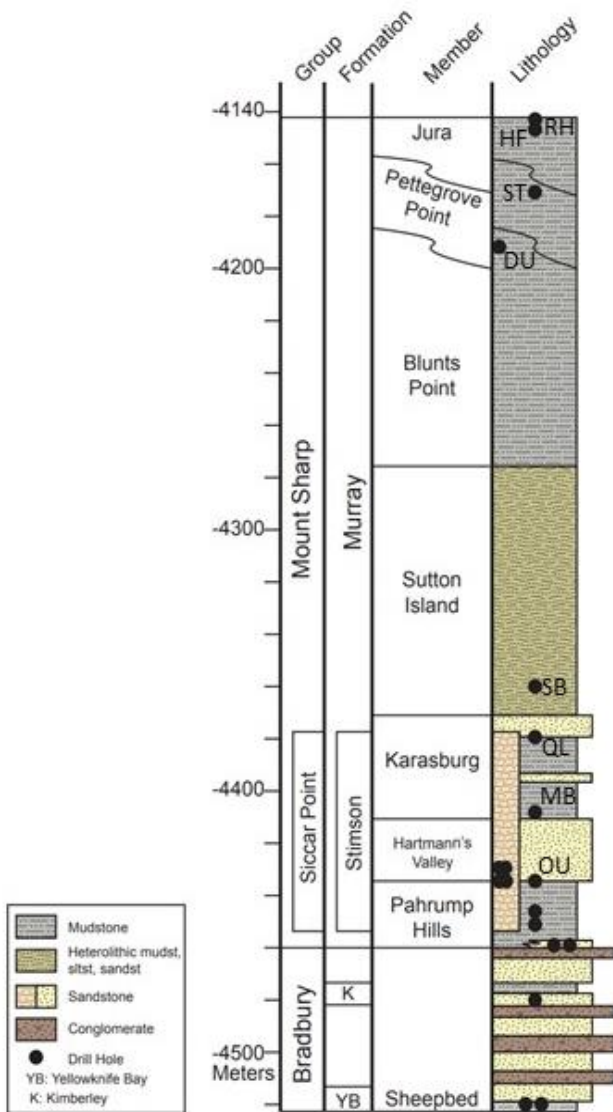
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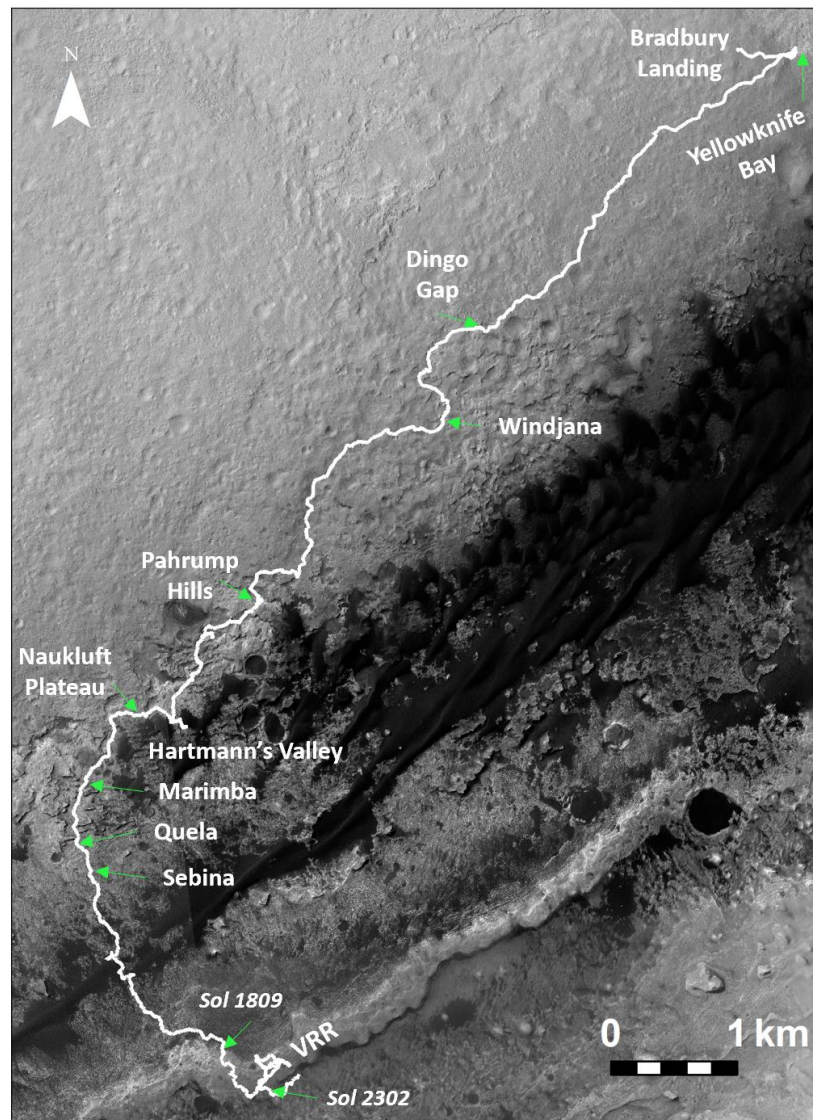


1378

1379 **Figure 1:** Stratigraphic column detailing the morphological characteristics of the stratigraphic
 1380 groups and units encountered by the *Curiosity* rover up to and including the Jura member. Drill
 1381 holes of interest in this study are annotated: Oudam (OU), Marimba (MB), Quela (QL), Sebina
 1382 (SB), Duluth (DU), Stoer (ST), Highfield (HF), and Rock Hall (RH). Image credit: The MSL
 1383 sedimentology and stratigraphy working group.

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1388 **Figure 2:** HiRISE orbital overview of the NASA Mars Science Laboratory *Curiosity* rover's
 1389 traverse from Bradbury Landing up to sol 2359. Select locations are annotated as well as sol
 1390 1809 when *Curiosity* ascended on to Vera Rubin ridge (VRR), and sol 2302 when *Curiosity*
 1391 traversed off VRR and into the Clay Bearing Unit. Adapted image from NASA-JPL/Fraeman.

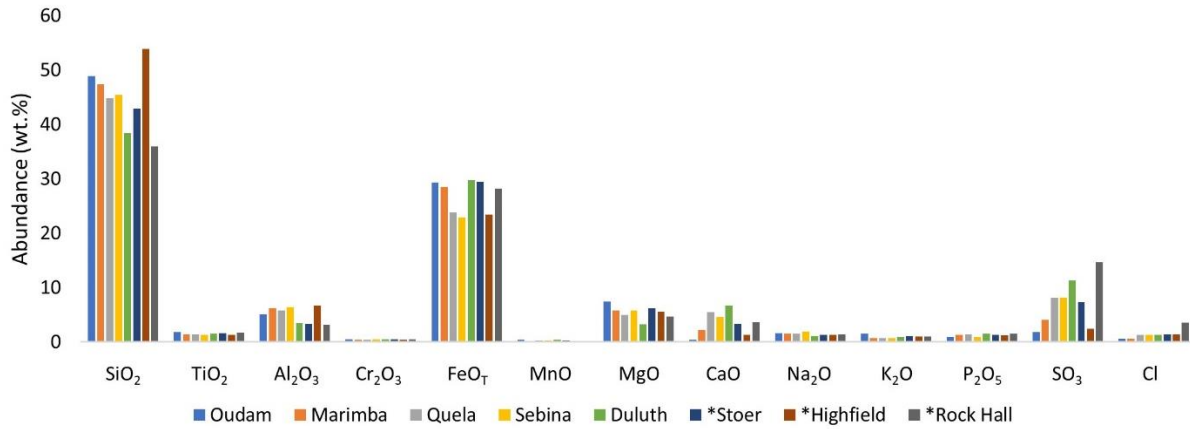
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1394 **Table 1:** Ratio of alteration to primary mineral content per drill hole, including and excluding
 1395 amorphous component as an alteration component. Ca-sulfates were excluded. Errors propagated
 1396 from uncertainty in CheMin mineral abundances. Pyroxenes and feldspars were considered to be
 1397 primary minerals. Fe-oxides, jarosite, quartz, halite, fluorapatite and phyllosilicates were
 1398 considered to be alteration. Source data take from Achilles et al. (2020) and Rampe et al.
 1399 (2020b).

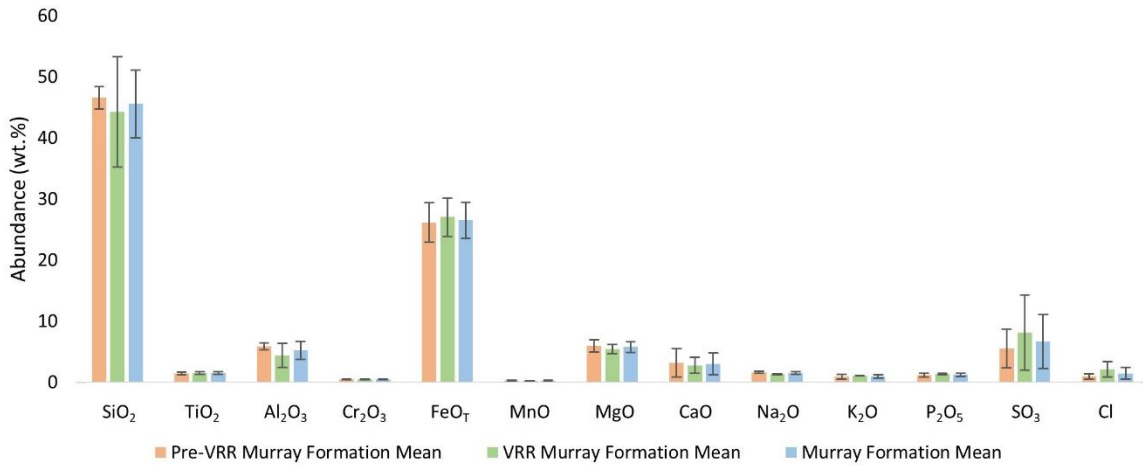
Drill hole	Including Amorphous	Excluding Amorphous
Oudam	2.1 ± 0.4	0.6 ± 0.1
Marimba	4.9 ± 0.8	2.3 ± 0.3
Quela	4.1 ± 0.8	1.3 ± 0.1
Sebina	5.3 ± 1.0	1.8 ± 0.2
Duluth	2.9 ± 0.3	0.8 ± 0.3
Stoer	2.3 ± 0.2	1.0 ± 0.2
Highfield	2.5 ± 0.2	0.6 ± 0.1
Rock Hall	2.0 ± 0.6	0.9 ± 0.2

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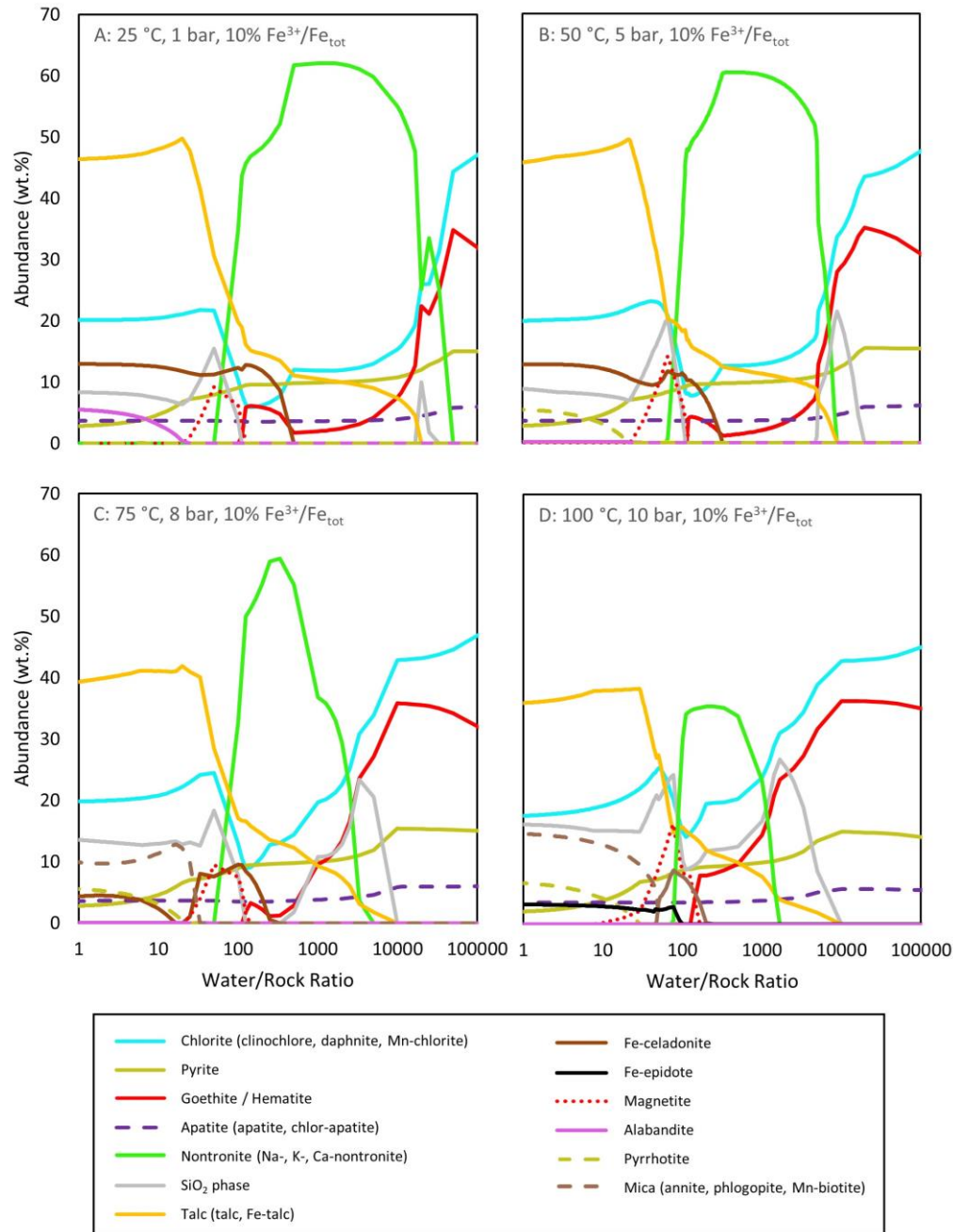
1402

1403 **Figure 3:** Main-phase alteration assemblage compositions for Oudam, Marimba, Quela, Sebina,
 1404 Duluth, Stoer, Highfield and Rock Hall. Calculated using APXS and CheMin results (Achilles et
 1405 al., 2020; Rampe et al., 2020b), as explained in methods section 2.2. Samples Oudam, Marimba,
 1406 Quela, Sebina, and Duluth are from pre-VRR Murray formation localities. Stoer, Highfield and
 1407 Rock Hall represent VRR Murray. *indicates drill samples acquired form VRR.
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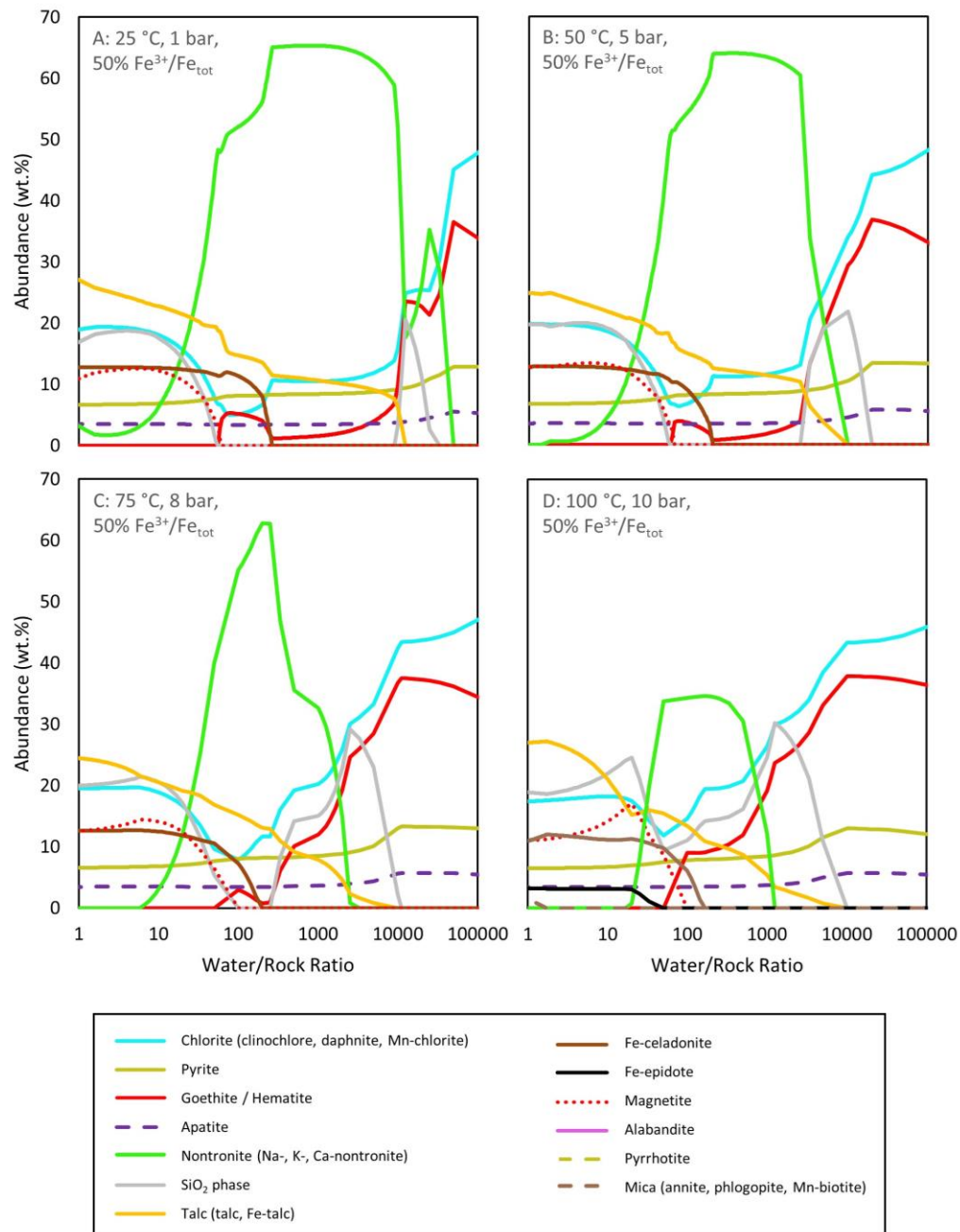
1409

1410 **Figure 4:** Mean alteration compositions for the Pre-VRR Murray formation (Oudam, Marimba,
 1411 Quela, Sebina), VRR Murray Formation (Stoer, Highfield and Rock Hall), the overall Murray
 1412 Formation. Calculated using APXS and CheMin results. Error bars show standard deviation for
 1413 each calculated mean, illustrating the statistical similarity between the calculated alteration
 1414 compositions.



1415

1416 **Figure 5:** CHIM-XPT results for the calculated VRR alteration composition (Table S4) reacted
 1417 with GPW (Bridges et al., 2015b). Reactions at 25, 50, 75 and 100 °C, and 10% of the FeO_T is
 1418 Fe³⁺, as indicated. Goethite only precipitated at 25 °C (A), and hematite did not precipitate at that
 1419 temperature. K-nontronite precipitated at 25 °C (A), whereas Na-nontronite did not precipitate at
 1420 100 °C (D) and Ca-nontronite precipitated at all temperatures. Chlor-apatite formed at 25 °C (A),
 1421 50 °C (B) and 75 °C (C), whereas apatite formed at 75 °C (C) and 100 °C (D). Trace abundances
 1422 of calcite, spurrite and merwinite are not included on the plots.



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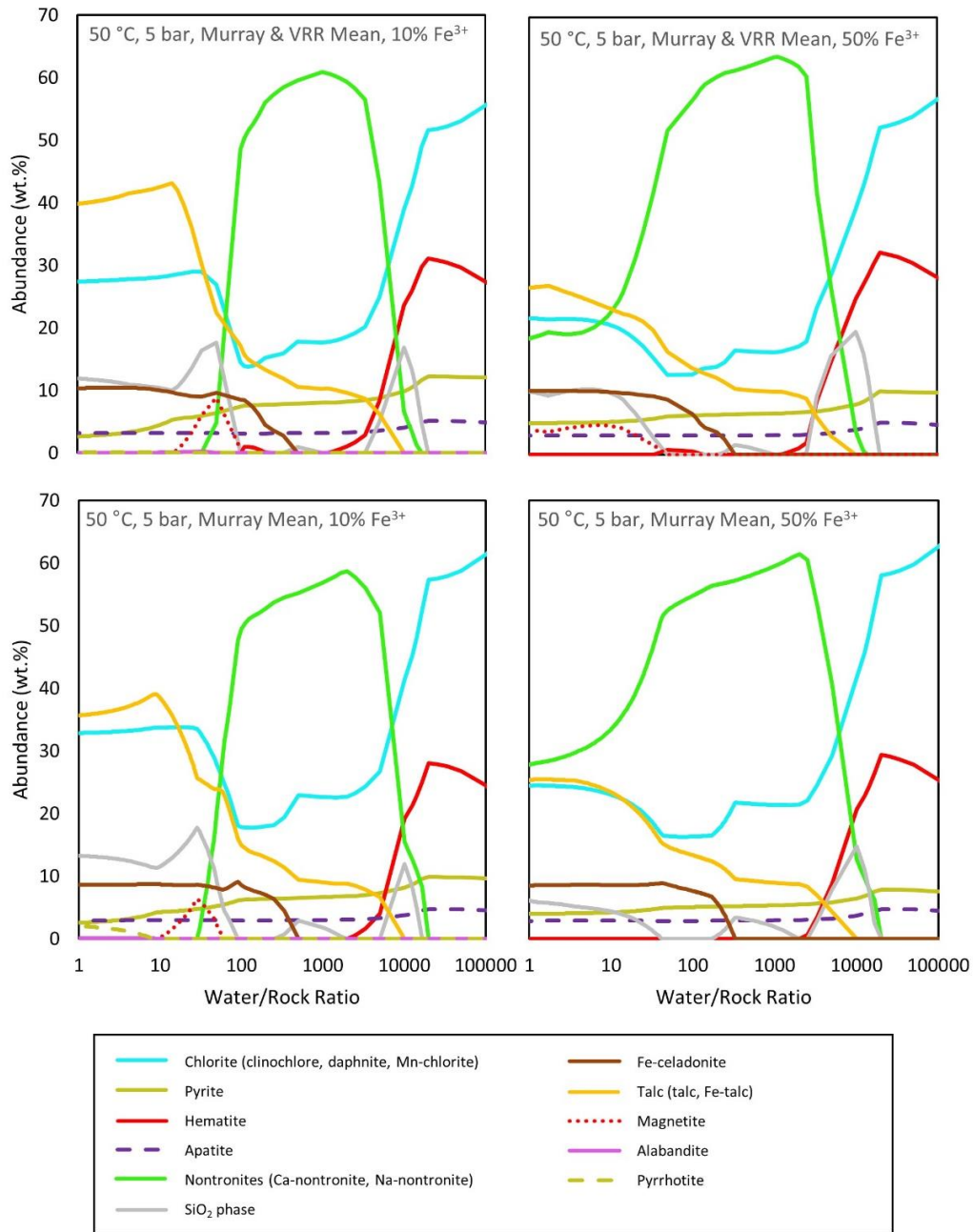
1424 **Figure 6:** CHIM-XPT results for the calculated VRR alteration composition (Table S4) reacted
 1425 with GPW (Bridges et al., 2015b). Reactions at 25, 50, 75 and 100 °C, and 50% of the FeO_T is
 1426 Fe³⁺, as indicated. Goethite only precipitated at 25 °C (A), and hematite did not precipitate at that
 1427 temperature. K-nontronite precipitated at 25 °C (A) and 50°C (B), whereas Na-nontronite did not
 1428 precipitate at 100 °C (D) and Ca-nontronite precipitated at all temperatures. Rhodochrosite
 1429 precipitated at 25 °C (A) and 50 °C (B), and trace wt.% of calcite precipitated at all temperatures
 1430 for 50% Fe³⁺/Fe_{tot} (A,B,C,D). Trace abundances of calcite, rhodochrosite, spurrite and merwinite
 1431 are not included on the plots.

1432

1433 **Table 2:** Summed VRR clay mineral wt.% / Fe-oxide wt.% ratio .% at high (10,000),
 1434 intermediate (1,000) and low (100) W/R ratios in thermochemical models (Figures 6 and 7)
 1435 using the calculated VRR mean alteration composition (Table S4) as the host rock (at both 10
 1436 and 50% Fe³⁺/Fe_{tot}) reacted with GPW (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using
 1437 CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot} Models			50% Fe ³⁺ /Fe _{tot} Models		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
25 °C	10.4	43.2	--	7.7	55.7	13.9
50 °C	1.2	40.7	--	1.2	46.0	21.4
75 °C	1.2	6.9	--	1.2	5.1	26.3
100 °C	1.2	3.8	--	1.1	2.3	6.9

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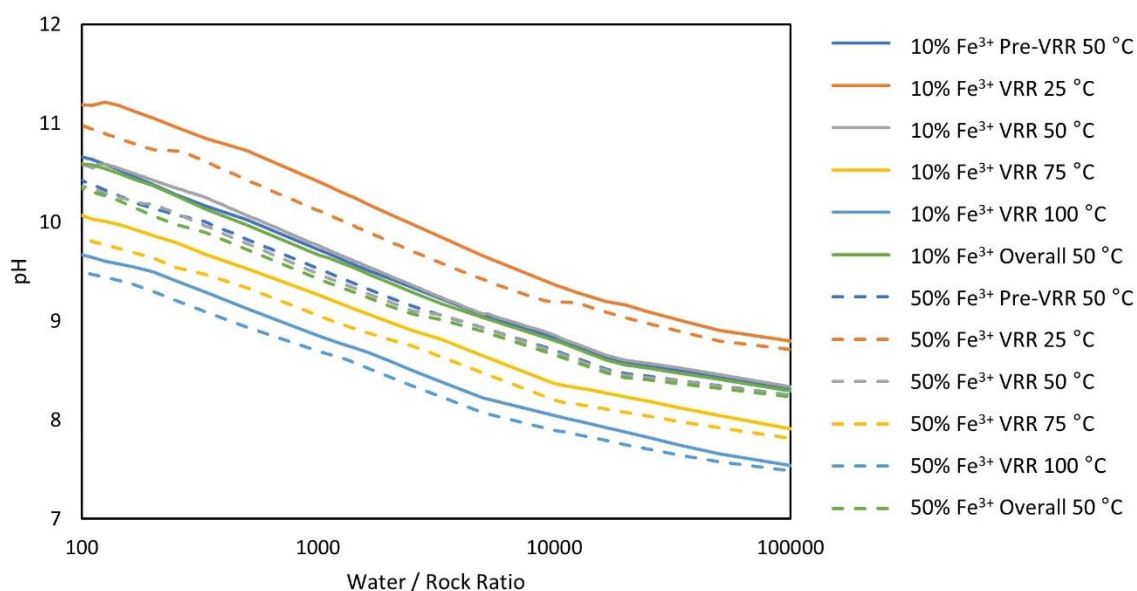
1440 **Figure 7:** CHIM-XPT results for the calculated alteration composition for the Murray formation
 1441 and the Murray and VRR (overall) (Table S4) reacted with GPW (Bridges et al., 2015b).

1442 Reactions are at 50 °C and the Fe³⁺ content of FeO_T is at 10 % and 50 %, as indicated. Trace
 1443 abundances of rhodochrosite, calcite, spurrite and merwinite are not included on the plot.
 1444

1445 **Table 3:** Summed clay wt.% / Fe-oxide wt.% ratio at high (10,000), intermediate (1,000) and low
 1446 (100) W/R ratios in models for the pre-VRR Murray mean and overall mean calculated alteration
 1447 compositions (Table S4) as the host rock, at 10 and 50% Fe³⁺/Fe_{tot}, reacted with GPW (Bridges
 1448 et al., 2015b) at 50 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot} Models			50% Fe ³⁺ /Fe _{tot} Models		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
Pre-VRR	3.0	--	--	2.6	--	--
Overall	1.9	--	--	1.7	--	--

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1451 **Figure 8:** Plot showing pH variation with W/R for the CHIM-XPT models shown in Figures 5, 6
 1452 and 7. Starting compositions for Pre-VRR Murray, VRR Murray and Overall Murray used in the
 1453 modeling are shown in Table S4.

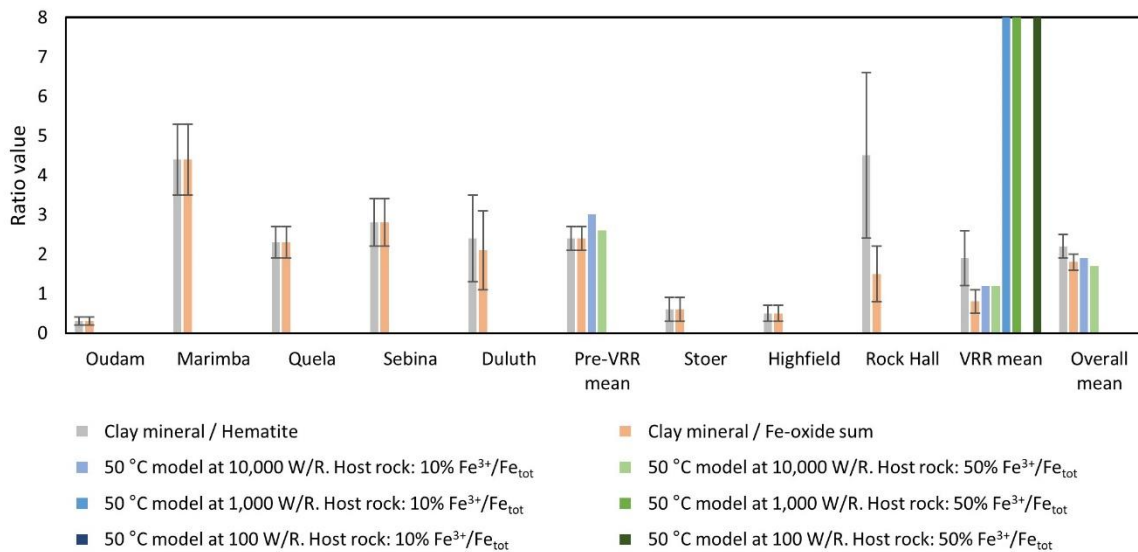
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1456 **Table 4:** Calculated clay mineral / hematite and clay mineral / Fe-oxide sum for drilled samples
 1457 in the pre-VRR Murray formation and VRR, determined using CheMin wt.% mineral
 1458 abundances (Achilles et al., 2020; Rampe et al., 2020b). Means are included for pre-VRR and
 1459 VRR samples, as well as an overall mean. Errors shown are propagated errors calculated from
 1460 errors in mineral abundances.

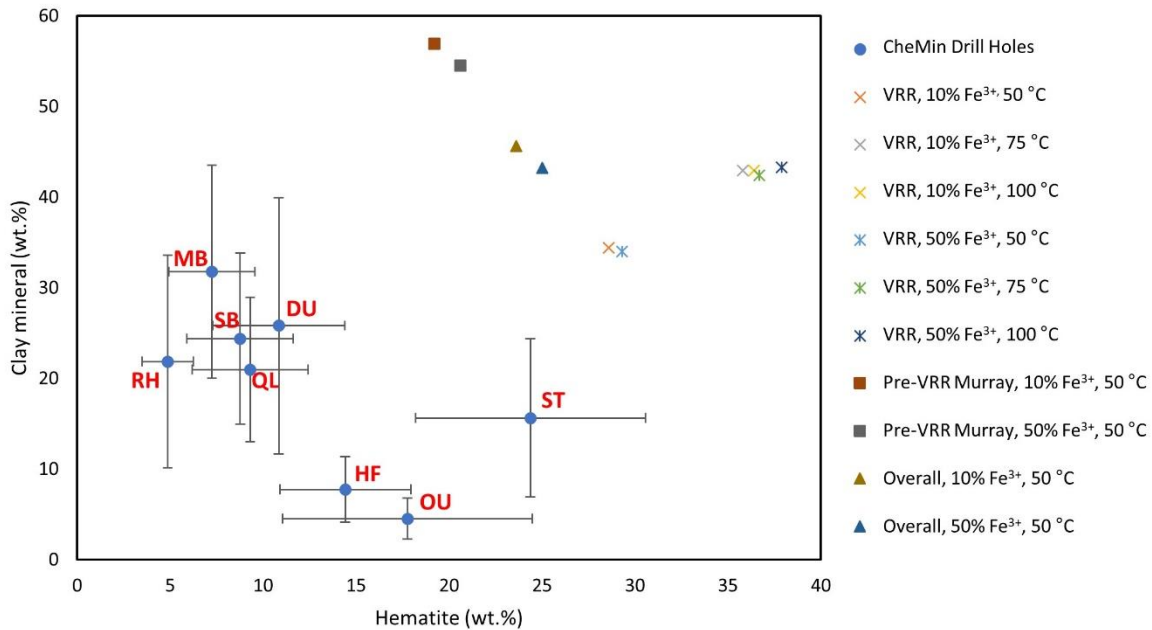
Drill Hole	Clay mineral / Hematite	Clay mineral / Fe-oxide sum
Oudam	0.3 ± 0.1	0.3 ± 0.1
Marimba	4.4 ± 0.9	4.4 ± 0.9
Quela	2.3 ± 0.4	2.3 ± 0.4
Sebina	2.8 ± 0.6	2.8 ± 0.6
Duluth	2.4 ± 1.1	2.1 ± 1.0
Pre-VRR mean	2.4 ± 0.3	2.4 ± 0.3
Stoer	0.6 ± 0.3	0.6 ± 0.3
Highfield	0.5 ± 0.2	0.5 ± 0.2
Rock Hall	4.5 ± 2.1	1.5 ± 0.7
VRR mean	1.9 ± 0.7	0.8 ± 0.3
Overall mean	2.2 ± 0.3	1.8 ± 0.2

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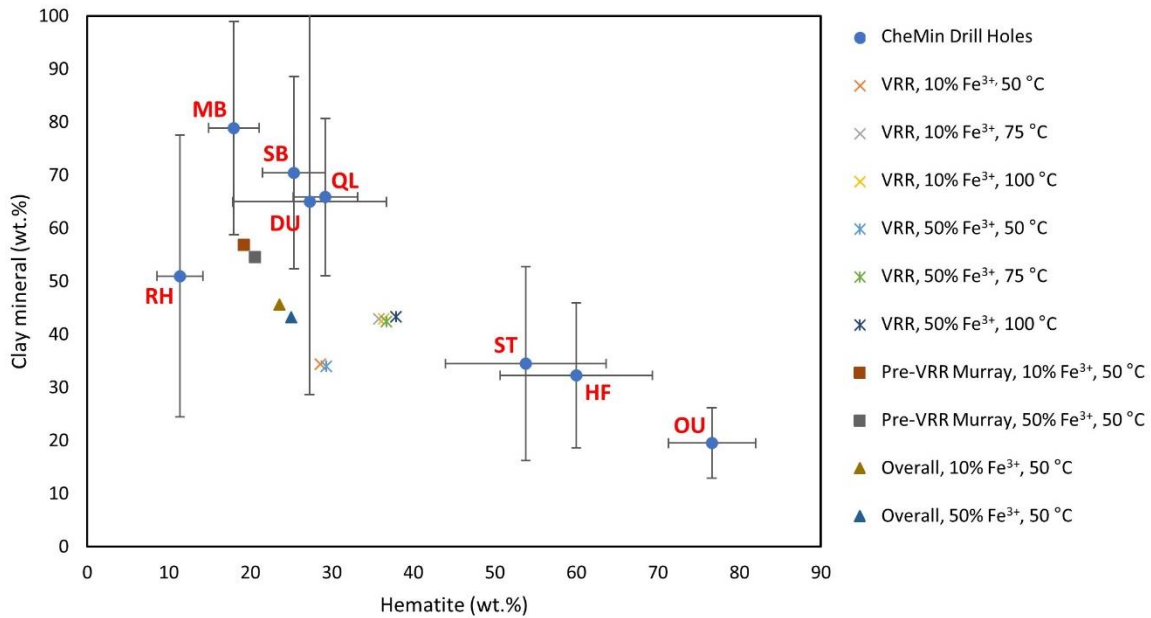
1462

1463 **Figure 9:** Plot comparing calculated clay mineral / hematite and clay mineral / Fe-oxide sum for
 1464 drill samples in the pre-VRR Murray formation and VRR, determined using CheMin wt.%
 1465 mineral abundances (Achilles et al., 2020; Rampe et al., 2020b). Means are included for pre-
 1466 VRR and VRR samples, as well as an overall mean. Errors shown are propagated errors
 1467 calculated from errors in mineral abundances. Values for models run at 50 °C at 10,000 W/R,
 1468 1,000 W/R and 100 W/R from Tables 2 and 3 are included for comparison.



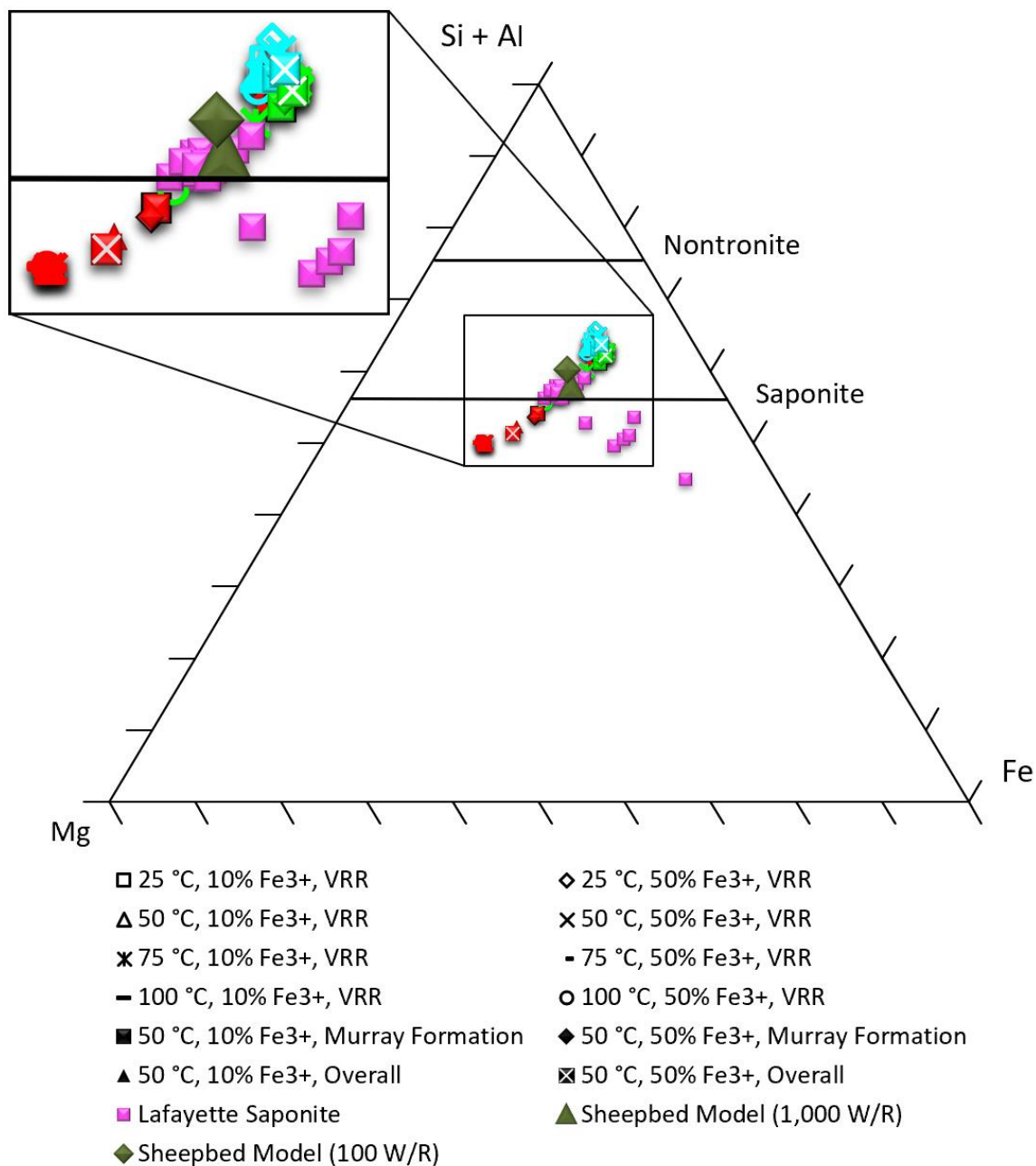
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1470 **Figure 10:** Clay mineral abundance vs hematite abundance from CheMin (Achilles et al., 2020;
 1471 Rampe et al., 2020b) normalized to the alteration component (including amorphous phase)
 1472 compared to CHIM-XPT results in this study (Figures 5, 6 and 7; Tables S5 and S8) at high
 1473 (10,000) W/R. Drill holes Oudam, Marimba, Quela, Sebina, Duluth, Stoer, Highfield and Rock
 1474 Hall are annotated with OU, MB, QL, SB, DU, ST, HF and RH, respectively. Linear regression
 1475 carried out on thermochemical models at 50 °C in the figure revealed the trend $y = (-2.35 \pm$
 1476 $0.09)x + (102.15 \pm 2.16)$ with an R^2 value of 0.99. Comparative linear regression carried out
 1477 on CheMin drill samples Oudam, Marimba, Sebina, Quela, Duluth, Highfield and Rock Hall in
 1478 the figure gave a trend of $y = (-1.88 \pm 0.56)x + (39.23 \pm 6.24)$ with an R^2 value of 0.70.
 1479 This trend changed to $y = (-2.56 \pm 0.45)x + (48.38 \pm 5.33)$ with an R^2 value of 0.89 with
 1480 Rock Hall removed from the analysis.



1481

1482 **Figure 11:** Clay mineral abundance vs hematite abundance from CheMin (Achilles et al., 2020;
 1483 Rampe et al., 2020b) normalized to the alteration component (excluding the amorphous
 1484 component) compared to CHIM-XPT results in this study (Figures 5, 6 and 7; Tables S5 and S8)
 1485 at high (10,000) W/R. The comparable negative correlations of different gradients for the
 1486 CheMin drill holes and the thermochemical models and the trend with temperature shown in
 1487 Figure 10 indicates that only a part of the derived alteration composition is reactive. Drill hole
 1488 names and abbreviations detailed in Figure 10 caption.



1489
 1490 **Figure 12:** Mg-Si+Al-Fe_{tot} at. ternary plot. Results at 10,000 (red), 1,000 (green) and 100 (blue)
 1491 W/R from the thermochemical models in this paper are plotted with some additional data from
 1492 other sources for comparison. Lafayette saponite data taken from Hicks et al. (2014). CHIM-
 1493 XPT results for the Sheepbed unit from Bridges et al. (2015b) at 100 W/R are shown for
 1494 comparison.

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1500 SUPPLEMENTARY MATERIAL

1501

1502 **Table S1.** Table outlining the crystal chemistries for the magmatic phases in Oudam, Marimba,
1503 Quela, Sebina, Duluth, Stoer, Highfield and Rock Hall.

Sample	Plagioclase	Alkali feldspar	Orthopyroxene
Oudam	An40(7) ^a	-	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Marimba	An39(5) ^a	K _{0.76(13)} Na _{0.24} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Quela	An39(6) ^a	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Sebina	An42(6) ^a	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Duluth	An34(4) ^d	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Stoer	An41(4) ^d	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Highfield	An28(3) ^d	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c
Rock Hall	An44(7) ^d	K _{0.65(18)} Na _{0.35} Al ₁ Si ₃ O ₈ ^b	Mg _{0.79(7)} Fe _{1.20(8)} Ca _{0.01(4)} Si ₂ O ₆ ^c

1504 ^a derived by Achilles et al. (2020). ^b values for average Murray formation for alkali feldspar derived by Morrison et
1505 al. (2018b). ^c values for average Yellowknife Bay for orthopyroxene derived by Morrison et al. (2018b). ^d derived by
1506 Rampe et al. (2020).

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1526 **Table S2.** Table detailing calculated alteration compositions for Oudam, Marimba, Quela, Sebina,
 1527 Duluth, Stoer, Highfield and Rock Hall. Errors propagated from APXS accuracy, uncertainty in
 1528 CheMin mineral abundances and uncertainties associated with magmatic phase crystal
 1529 chemistry. Source data take from Achilles et al. (2020) and Rampe et al. (2020).

	Oudam	Marimba	Quela	Sebina
SiO ₂	48.83 ± 2.55	47.33 ± 1.32	44.85 ± 1.47	45.38 ± 1.44
TiO ₂	1.77 ± 0.07	1.37 ± 0.04	1.38 ± 0.05	1.30 ± 0.04
Al ₂ O ₃	5.08 ± 0.49	6.18 ± 0.40	5.79 ± 0.49	6.45 ± 0.39
Cr ₂ O ₃	0.54 ± 0.02	0.42 ± 0.01	0.38 ± 0.01	0.45 ± 0.02
FeO _T	29.30 ± 0.98	28.47 ± 0.61	23.79 ± 0.56	22.91 ± 0.70
MnO	0.37 ± 0.02	0.11 ± 0.01	0.29 ± 0.01	0.25 ± 0.01
MgO	7.42 ± 0.40	5.74 ± 0.25	4.99 ± 0.18	5.75 ± 0.31
CaO	0.40 ± 0.65	2.19 ± 0.38	5.47 ± 0.32	4.57 ± 0.30
Na ₂ O	1.56 ± 0.26	1.51 ± 0.12	1.51 ± 0.21	1.89 ± 0.20
K ₂ O	1.46 ± 0.08	0.71 ± 0.12	0.65 ± 0.10	0.71 ± 0.08
P ₂ O ₅	0.88 ± 0.09	1.34 ± 0.09	1.45 ± 0.10	0.86 ± 0.07
SO ₃	1.81 ± 0.31	4.02 ± 0.47	8.14 ± 0.27	8.12 ± 0.32
Cl	0.59 ± 0.02	0.61 ± 0.03	1.33 ± 0.03	1.35 ± 0.26

	Duluth	Stoer	Highfield	Rock Hall
SiO ₂	38.34 ± 1.33	42.91 ± 2.24	53.84 ± 2.18	35.91 ± 3.25
TiO ₂	1.49 ± 0.05	1.64 ± 0.06	1.31 ± 0.05	1.69 ± 0.09
Al ₂ O ₃	3.49 ± 0.34	3.36 ± 0.64	6.66 ± 0.59	3.10 ± 1.09
Cr ₂ O ₃	0.48 ± 0.04	0.46 ± 0.05	0.42 ± 0.05	0.52 ± 0.03
FeO _T	29.71 ± 0.86	29.46 ± 0.99	23.46 ± 1.07	28.19 ± 2.28
MnO	0.36 ± 0.04	0.27 ± 0.02	0.22 ± 0.02	0.13 ± 0.02
MgO	3.28 ± 0.31	6.17 ± 0.36	5.54 ± 0.44	4.65 ± 1.11
CaO	6.72 ± 0.37	3.32 ± 0.67	1.29 ± 0.54	3.67 ± 1.17
Na ₂ O	1.09 ± 0.20	1.25 ± 0.25	1.28 ± 0.24	1.40 ± 0.28
K ₂ O	0.93 ± 0.11	1.10 ± 0.27	1.01 ± 0.13	1.05 ± 0.06
P ₂ O ₅	1.56 ± 0.10	1.31 ± 0.08	1.17 ± 0.08	1.47 ± 0.10
SO ₃	11.25 ± 0.45	7.30 ± 0.85	2.44 ± 0.72	14.69 ± 1.55
Cl	1.30 ± 0.05	1.45 ± 0.06	1.37 ± 0.07	3.54 ± 0.16

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1542 **Table S3.** Table detailing rationale for minerals prevented from forming in CHIM-XPT (Reed et al., 2010)
 1543 thermochemical modelling. For acmite, akermanite, antigorite, Fe-anthophyllite, ferro-actinolite, bredigite,
 1544 grunerite, jennite, pyroxmangite, riebeckite, tobermorite, tremolite, wollastonite see Melwani Daswani et al. (2016).

Mineral	Rationale	Reference
Al-free_chlorite	Caused convergence issues during modeling.	

Belite	Industrial mineral in cement.	Tantawy et al., 2014
Clinozoisite	Clinozoisite-epidote series, members occur from ~130 bar and 320°C.	Deer et al., 2013 and references therein
Deerite	Forms from 200 °C and 8 kbar.	Vernié et al., 1986 and references therein
Diopside	Ca clinopyroxene. In series with hedenbergite.	Deer et al., 2013 and references therein
Epidote, Fe-epidote	Clinozoisite-epidote series, members occur from ~130 bar and 320°C.	Deer et al., 2013 and references therein
Hedenbergite	Ca clinopyroxene. In series with diopside.	Deer et al., 2013 and references therein
Larnite-bredigite	Solid solution of larnite and bredigite. Ca-silicate. Forms in contact metamorphism of carbonates.	Melwani Daswani et al., 2016 and references therein.
Prehnite	Forms at 200-300 °C.	Robinson & Bevans, 1999
Rankinite	High temperature Ca-silicate phase.	Treiman & Essene, 1983
Rhodonite	Pyroxenoid	Pinckney & Burnham, 1988
Tephroite	Mn-olivine	Deer et al., 2013 and references therein
Tilleyite	Occurs in contact metamorphic zone between igneous rocks and limestones. Low pressure, high-T.	Harker, 1959
tr.625ac.25prg.125	Solid solution of tremolite, actinolite and paragonite	Melwani Daswani et al., 2016 and references therein
Vesuvianite	Requires T > 360 °C and P> 50 bar.	Deer et al., 2013 and references therein

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1555 **Table S4.** Details of mean alteration compositions for the Murray formation, VRR, and an overall
1556 composition. Errors propagated from APXS accuracy errors, uncertainty in CheMin mineral
1557 abundances and uncertainties associated with magmatic phase crystal chemistry. Standard
1558 deviations for each mean is also detailed. Source data take from Achilles et al. (2020) and Rampe
1559 et al. (2020).

	Pre-VRR Murray*		VRR Murray		Overall*	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
SiO ₂	46.60 ± 3.48	1.83	44.22 ± 4.79	9.04	45.58 ± 5.72	5.52
TiO ₂	1.45 ± 0.10	0.21	1.55 ± 0.12	0.21	1.49 ± 0.16	0.20
Al ₂ O ₃	5.87 ± 0.92	0.60	4.37 ± 1.70	1.99	5.23 ± 1.66	1.46
Cr ₂ O ₃	0.45 ± 0.03	0.07	0.47 ± 0.07	0.05	0.46 ± 0.08	0.06
FeO _T	26.12 ± 1.45	3.23	27.04 ± 2.73	3.16	26.51 ± 3.08	2.97

MnO	0.25 ± 0.04	0.11	0.21 ± 0.04	0.07	0.24 ± 0.04	0.09
MgO	5.97 ± 0.56	1.03	5.45 ± 1.27	0.76	5.75 ± 1.38	0.89
CaO	3.16 ± 5.19	2.30	2.76 ± 2.12	1.29	2.99 ± 1.69	1.80
Na ₂ O	1.62 ± 0.41	0.18	1.31 ± 0.42	0.08	1.49 ± 0.60	0.21
K ₂ O	0.88 ± 0.23	0.39	1.05 ± 0.29	0.04	0.96 ± 0.36	0.29
P ₂ O ₅	1.13 ± 0.18	0.30	1.32 ± 0.16	0.15	1.21 ± 0.23	0.25
SO ₃	5.52 ± 1.19	3.14	8.14 ± 3.00	6.17	6.64 ± 2.03	4.43
Cl	0.97 ± 0.20	0.43	2.12 ± 0.15	1.23	1.46 ± 0.32	0.99

*Not including Duluth.

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Table S5. Hematite wt.% at high (10,000), intermediate (1,000) and low (100) W/R ratios in thermochemical models (Figures 5 and 6) and using the calculated VRR mean alteration composition (Table S4) as the host rock (at both 10 and 50% Fe³⁺/Fe_{tot}) reacted with GPW (Bridges et al., 2015b) at 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot} Models			50% Fe ³⁺ /Fe _{tot} Models		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
50 °C	28.6	2.1	0.0	29.3	1.9	3.6
75 °C	35.8	9.6	0.0	36.7	12.0	3.0
100 °C	36.4	14.5	0.0	37.9	19.2	9.0

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Table S6. Pyrite wt.% at high (10,000), intermediate (1,000) and low (100) W/R ratios in thermochemical models (Figures 5 and 6) using the calculated VRR mean alteration composition (Table S4) as the host rock (at both 10 and 50% Fe³⁺/Fe_{tot}) reacted with GPW (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot} Models			50% Fe ³⁺ /Fe _{tot} Models		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
25 °C	10.8	9.9	9.0	9.2	8.4	8.1
50 °C	12.4	10.0	4.6	10.5	8.5	8.1
75 °C	15.4	10.0	9.0	13.0	8.5	8.1
100 °C	15.1	10.0	8.8	13.1	8.5	7.9

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1587 **Table S7.** Summed nontronite wt.% at high (10,000), intermediate (1,000) and low (100) W/R
1588 ratios in thermochemical models (Figures 5 and 6) using the calculated VRR mean alteration
1589 composition (Table S4) as the host rock (at both 10 and 50% Fe³⁺/Fe_{tot}) reacted with GPW
1590 (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot} Models			50% Fe ³⁺ /Fe _{tot} Models		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
25 °C	55.1	62.0	38.2	52.2	65.3	52.1
50 °C	0.0	60.1	33.5	0.0	63.3	54.5
75 °C	0.0	36.8	32.5	0.0	32.7	52.2
100 °C	0.0	23.4	30.2	0.0	12.2	34.3

1591 **Table S8.** Summed clay wt.% at high (10,000), intermediate (1,000) and low (100) W/R ratios in
1592 models for the VRR mean composition (Table S4), at both 10 and 50% Fe³⁺/Fe_{tot}, reacted with
1593 GPW (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot}			50% Fe ³⁺ /Fe _{tot}		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
25 °C	77.8	84.5	64.9	74.3	86.5	71.9
50 °C	34.4	84.3	63.5	34.0	86.2	76.2
75 °C	42.9	65.8	62.6	42.4	60.8	78.2
100 °C	42.9	54.9	60.9	43.3	43.9	62.4

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1595 **Table S9.** Summed chlorite wt.% at high (10,000), intermediate (1,000) and low (100) W/R ratios
1596 in models for the VRR mean composition (Table S4), at both 10 and 50% Fe³⁺/Fe_{tot}, reacted with
1597 GPW (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot}			50% Fe ³⁺ /Fe _{tot}		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R

25 °C	15.1	11.9	10.4	15.8	10.5	5.1
50 °C	34.4	12.9	11.5	34.0	11.5	6.7
75 °C	42.9	19.7	13.0	42.4	20.2	7.9
100 °C	42.9	23.8	15.0	43.3	15.0	14.7

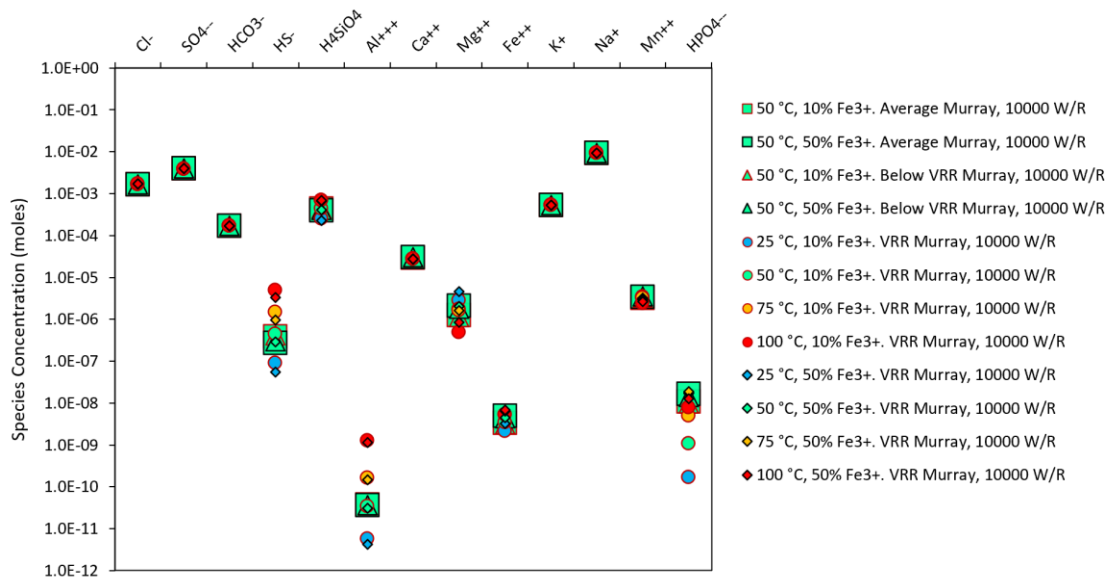
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1599 **Table S10.** Summed talc wt.% at high (10,000), intermediate (1,000) and low (100) W/R ratios in
 1600 models for the VRR mean composition (Table S4), at both 10 and 50% Fe³⁺/Fe_{tot}, reacted with
 1601 GPW (Bridges et al., 2015b) at 25, 50, 75 and 100 °C using CHIM-XPT (Reed et al., 2010).

	10% Fe ³⁺ /Fe _{tot}			50% Fe ³⁺ /Fe _{tot}		
	10,000 W/R	1,000 W/R	100 W/R	10,000 W/R	1,000 W/R	100 W/R
25 °C	7.4	10.5	19.8	6.3	10.6	14.7
50 °C	0.0	11.4	18.4	0.0	11.3	14.9
75 °C	0.0	9.3	17.1	0.0	7.9	15.2
100 °C	0.0	7.7	15.8	0.0	5.4	13.5

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1606 **Figure S1.** Modeled fluid composition at high (10000) W/R for all three alteration derived alteration compositions
 1607 (Table S4) for all modeled temperatures and Fe³⁺/Fe_{tot}.

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