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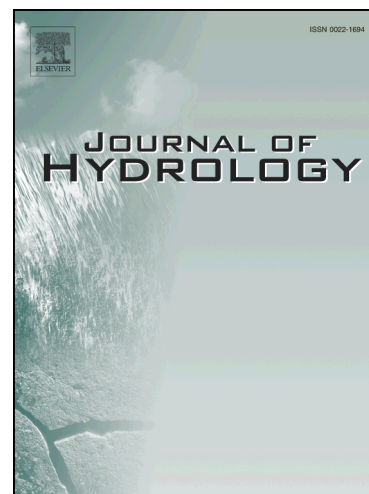
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**Controls on dripwater chemistry of Oregon Caves National Monument,  
northwestern United States**

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21 **Abstract**

22 Cave dripwater chemistry of Oregon Caves National Monument (OCNM) was  
23 studied, where the parameters pH, total alkalinity, calcium, magnesium, strontium,  
24 sodium and barium were analyzed at quasi-monthly intervals from 2005 to 2007.  
25 Different statistical analyses have been used to investigate the variability of the chemical  
26 parameters in the different sites in the OCNM cave system. The dripwater varies in  
27 response to seasonal changes in rainfall. The drip rates range from zero in summer to  
28 continuous flow in winter, closely following the rainfall intensity. Spatial variations of  
29 dripwater chemistry, which is nonlinearly related to dripwater discharge likely, reflect the  
30 chemical composition of bedrock and overlying soil, and the residence time of the ground  
31 water within the aquifer. The residence time of infiltrated water in bedrock cracks control  
32 the dissolution carbonate bedrock, reprecipitation of calcium carbonate and the degree of  
33 saturation of dripwater with respect to calcium carbonate minerals. Spatiotemporal  
34 fluctuations of dripwater Mg/Ca and Sr/Ca ratios are controlled by dissolution of  
35 carbonate bedrock and the degree of calcite reprecipitation in bedrock cracks. This  
36 suggests that trace elements in speleothem deposits at the OCNM may serve as  
37 paleoclimatological proxies for precipitation, if interpreted within the context of  
38 understanding local bedrock chemistry.

39

40 **Keywords:** OCNM, Oregon, speleothem, geochemistry, dripwater, Mg/Ca, Sr/Ca

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## 44 1. Introduction

45 Interactions between rain, soil, and bedrock produce a variety of biogeochemical  
46 signals in cave dripwaters including  $\delta^{18}\text{O}$  and  $\delta\text{D}$  from rain, traces of organic matter,  $\delta^{13}\text{C}$   
47 of total dissolved  $\text{CO}_2$  and elements such as calcium, magnesium, strontium. Dripwater  
48 properties depend on the surrounding environmental conditions and on the dissolution  
49 and precipitation processes in the karst system (Fairchild et al., 2000; 2006; Toran and  
50 Roman, 2006; Borsato et al., 2015; Casteel and Banner, 2015; Zeng et al., 2015). Studies  
51 of limestone caves identified seasonal variations in ionic concentrations of dripwaters  
52 (Baker et al., 2000; Drever, 1982; Musgrove and Banner, 2004; Day and Henderson,  
53 2013). For example, total dissolved ion concentrations in dripwaters were observed to  
54 correlate with soil  $\text{CO}_2$  seasonal variations (Mayer, 1999) because higher levels of soil  
55  $\text{CO}_2$  increase carbonate mineral dissolution. The composition of the host rock also  
56 strongly influences the water composition (Motyka et al., 2005; Smart et al., 1986; Tooth  
57 and Fairchild, 2003). Dripwaters with high concentrations of calcium and bicarbonate are  
58 mainly produced from calcitic bedrock while waters with high concentrations of calcium,  
59 magnesium, bicarbonate, and sulfate are produced from dolomitic bedrock with pyrite  
60 (Chalmin et al., 2007; Bar-Matthews et al., 1991; Frisia et al., 2002; Wu et al., 2015). The  
61 variation in physical and chemical properties of dripwater may be incorporated and  
62 preserved in speleothem deposits, and these changes have been used to infer paleoclimate  
63 and paleoenvironmental conditions in the caves where speleothem deposits were formed  
64 (McDermott, 2004; Fairchild et al., 2006; Johnson et al., 2006; McDonald et al., 2007;  
65 Lachniet 2009, Steponaitis et al., 2015). The physicochemical characteristics of the drip  
66 waters can help in understanding the processes that affect the formation of stalagmites

67 and carbon, hydrogen and oxygen isotopic composition (McDonald et al., 2007; Lambert  
68 and Aharon, 2011).

69 Drip water rates change seasonally and vary from slow and irregular to fast and  
70 continuous (Baker and Brunson, 2003; Baker et al., 2000; Fernández-Cortés et al., 2007).  
71 The drip water rates in the Oregon Caves National Monument (OCNM) also vary  
72 seasonally and range from slow to no drip at shallow rooms to fast and constant drip at  
73 the deeper rooms (Schubert 2007). The control of drip water rate and room locality (i.e.,  
74 shallow vs depth) on the drip water chemistry has not been fully investigated. Therefore,  
75 the objectives of this work were to: (1) characterize the geochemistry and the saturation  
76 states of the waters with respect to carbonate minerals and (2) investigate the possible  
77 factors that control dripwater chemistry and their potential influence on the chemical  
78 composition of speleothems from shallow (slow dripwater rate) and deep (fast dripwater  
79 rate) rooms. Here, we analyze dripwaters from the OCNM in southwestern Oregon of the  
80 USA.

81

## 82 **2. Study Area and Sampling Sites**

83 The OCNM is located in the Klamath Mountains, southwestern Oregon (42° 05'  
84 53" N, 123° 24' 26" W, altitude ~1220m) (Fig. 1). The modern vegetation above the cave  
85 is dominated by *Pseudotsuga menziesii* (Douglas fir) and *Abies concolor* (white fir). The  
86 plants are mainly of C-3 type vegetation. Soils overlying the OCNM are from various  
87 bedrock lithologies including granites and serpentinites. The bedrock in the OCNM cave  
88 system belongs to the Paleozoic-Triassic Applegate Group, consisting of metavolcanics  
89 and metasediments (Irwin, 1966; Barnes et al., 1996). The OCNM was formed in a

90 faulted and folded marble lens, and was carved by meteoric waters that have percolated  
91 through the overlying soil and bedrock (Barnes et al., 1996; Vacco et al., 2005; Schubert,  
92 2007).

93 The measured temperature deep inside the cave is approximately constant through  
94 the year at  $8.8 \pm 0.7^\circ\text{C}$ . The monthly-average temperature outside the cave ranges from  
95  $\sim 19^\circ\text{C}$  in summer to  $\sim 6.5^\circ\text{C}$  in winter (Schubert, 2007). Precipitation falls mostly as rain  
96 in the fall and spring and as snow in winter, but is virtually absent in summer (Taylor and  
97 Hannan, 1999). Water entering the cave is derived from local snowmelt and rainfall  
98 (Ersek et al., 2010). Rainfall events activate dripwater sites within hours to days in the  
99 upper part of the cave, although water also may take months to years to reach the cave  
100 through cracks parallel to the orientation of the bedrock structure (Roth, 2005). While  
101 upper parts of the cave dry out by the end of summer, deeper parts remain wet throughout  
102 the year (Schubert, 2007).

103

### 104 **3. Methodology**

#### 105 3.1. Sampling

106 Dripwater samples were collected at four sites within the OCNM cave system  
107 (Fig. 1) at quasi-monthly intervals from January, 2005 to July, 2007. We collected the  
108 water samples manually and used a stopwatch to count the number of drips/minute. We  
109 did this 3 times and averaged the number. Precipitation data were obtained from a  
110 weather station installed outside the cave. Collection sites were situated in the the Kings  
111 and Queens Throne Room (KQR,  $\sim 14$  meters subsurface), Imagination Room (IR,  $\sim 18$  m  
112 subsurface), the Miller's Chapel Room (MR,  $\sim 30$  m subsurface), and from two sites in

113 the Shower Room (SR1 and SR2, ~51 m subsurface). All water samples were collected  
114 into dark amber glass bottles with airtight screw-cap seals and plastic vapor barriers  
115 which were acid-washed, rinsed with deionized water purified with Milli-Q Plus Water  
116 System (Millipore) prior to use. Nitric acid was added to each sample to achieve pH ~ 1.0  
117 (Cenci and Martin, 2004).

118 . The samples were subsequently stored in a refrigerator for 1-12 months before  
119 analysis, where the pH and total alkalinity measurements were performed during the first  
120 2-3 months of the sample collection. The analyses of trace and major elements were  
121 conducted 3-6 months later.

### 123 3.2. Chemical Analyses

124 The bottles were carefully sealed to ensure that they remain gas-tight to prevent  
125 any atmospheric gas exchange. We divided the water samples into two aliquots. The first  
126 aliquot, which was drawn slowly from the top 5 cm of the solution, was used for pH and  
127 total alkalinity measurements, and the second aliquot was used for isotopic (Ersek et al.,  
128 2010) and major and minor element analyses. As sample pH can be affected by gas  
129 exchange, the pH and total alkalinity measurements were performed in closed cell to  
130 avoid any opportunity to CO<sub>2</sub> exchange with atmosphere.

131 pH Benchtop meter (Thermo Scientific™ Orion Star™ A211) was used to  
132 measure pH and total alkalinity. Before proceeding with any pH and titration  
133 measurements, we standardized the electrodes in two VWR buffer solutions assigned pH  
134 of  $4.63 \pm 0.02$  at 25°C ( $4.62 \pm 0.02$  at 20°C) and pH of  $7.38 \pm 0.02$  at 25°C ( $7.39 \pm 0.02$  at  
135 20°C), and determined the slope, S, of the electrode, expressed in mv/pH. We compared



136 the slope with the theoretical one (e.g.,  $S = 58.178$  mv/pH at  $20^{\circ}\text{C}$ ) and if measurements  
137 were within 1%, the theoretical value was usually used. The practical slope for six  
138 different measurements had a standard deviation of  $\pm 0.099$  mv/pH and % error ranged  
139 from -0.325 to 0.117%. The measured pH,  $\text{pH}_m$ , was calculated from:

140

$$141 \quad \text{pH}_m = \text{pH}_b + \frac{E_m - E_b}{S} \quad (1)$$

142

143 where  $\text{pH}_b$  is the pH of the standard buffer solution, and  $E_m$  and  $E_b$  are the electrode  
144 potential in the test solution and in the standard buffer, respectively. No significant drift  
145 in pH electrode was observed during the routine measurements. The reproducibility of  
146 the pH measurements was found to range from 0.009-0.024pH unit at  $\text{pH} > 7.50$  and  
147 from 0.005-0.013pH unit for  $\text{pH} < 4.00$ .

148 Total alkalinity (TA) of each test solution was measured using the Gran titration  
149 method (Gran, 1952; Dyrssen and Sillen, 1967; Mehrbach et al, 1973; Rushdi et al.,  
150 1998). The standard deviation of total alkalinity was  $\pm 5.8$   $\mu\text{eq L}^{-1}$  solution.

151 We analyzed major and trace metals by inductive coupled plasma-mass  
152 spectrometry at the W.M. Keck Collaboratory, College of Oceanic and Atmospheric  
153 Sciences, Oregon State University. The metals (and their detection limits) included  
154 calcium (Ca) (0.1 ppm), magnesium (Mg) (0.4 ppb), strontium (Sr) (0.1 ppb), barium (Ba)  
155 (0.1 ppb), and sodium (Na) (3 ppb). Deionized water was used to prepare the calibration  
156 and quality control solutions. Nitric acid was added to the matrix of the standard and  
157 quality control solutions to achieve  $\text{pH} \sim 1.0$ . We analyzed reference solutions every 10-  
158 20 samples to monitor the stability of analytical system. Standard deviations of triplicate

159 analyses were better than <5%. The concentrations of potassium ( $K^+$ ), chlorine ( $Cl^-$ ) and  
 160 sulfate ( $SO_4^{2+}$ ) ions were obtained from the data of a different project, studying the  
 161 dripwater chemistry of same rooms, by Schubert (2007).

162

### 163 3.3. Degree of saturation with respect to carbonate minerals

164 The saturation states of the solutions are calculated at in situ temperatures using  
 165 the ratio of ionic products (IP) to solubility constants ( $K_{sp}$ ) of the mineral of interest (i.e.,  
 166 IP/ $K_{sp}$ ). This value is known as degree of saturation ( $\Omega$ ), saturation ratio, and saturation  
 167 index (SI) (Picknett et al., 1976). The percent degree of saturation ( $\% \Omega$ ) with respect to  
 168 different carbonate minerals was calculated from:

169

$$170 \quad \% \Omega = \left[ \frac{(Ca^{2+})_T * CA \frac{K_2}{(\gamma_{H^+})_T (H^+)_T + 2K_2}}{\frac{K_{sp}^0}{(\gamma_{Ca^{2+}})_T (\gamma_{CO_3^{2-}})_T}} \right] * 100 \quad (2)$$

171

$$172 \quad K_2 = \frac{K_2^0 (\gamma_{HCO_3^-})_T}{(\gamma_{H^+})_T (\gamma_{CO_3^{2-}})_T} \quad (3)$$

173

174 where CA is the carbonate alkalinity ( $CA = (HCO_3^-) + (CO_3^{2-})$ );  $(\gamma_i)_T$  is the total activity  
 175 coefficient of the species  $(i)_T$  (Davies, 1962); and  $K_2$  and  $K_2^0$  are the second  
 176 stoichiometric and thermodynamic dissociation constants of carbon acid (Hanred and  
 177 Scholes 1941);  $K_{sp}$  and  $K_{sp}^0$  are the stoichiometric and thermodynamic solubility  
 178 constants of the mineral calcium carbonate, respectively (Plummer and Bunsenberg,

179 1982). The concentration ranges of  $\text{Cl}^-$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  of the dripwaters (Schurbet, 2007)  
180 were small relative to  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and did not affect the computed values of  
181  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  activity coefficients; thus, their concentration effects on the saturation  
182 states of calcium carbonate minerals are insignificant.

183 Values of  $\% \Omega$  were estimated for pure calcite, aragonite, and vaterite minerals.  
184 Our calculation was in a good agreement with the values estimated by Schubert (2007)  
185 using PHREEQC1 speciation water resource application software (Parkhurst, 2000).

186

### 187 3.4. Statistical analysis

188 The statistical analyses including linear relationships between different physical  
189 and chemical parameters, cluster analysis (CA) and principal component analysis (PCA)  
190 were performed using the SPSS (IBM-Statistical Package for the Social Sciences, version  
191 16.0).

192

## 193 **4. Results and discussion**

### 194 4.1. Rainfall and Dripwater rates

195 In 2005, precipitation was up to 25.1 millimeter per month ( $\text{mm m}^{-1}$ ), with  
196 maximum rain occurring in October. The amount of precipitation increased in 2006 with  
197 a maximum amount in November ( $276.9 \text{ mm m}^{-1}$ ) and December ( $368.3 \text{ mm m}^{-1}$ ) (Fig. 2).  
198 The increase in the amount of precipitation was also significant in 2007, where the  
199 maximum rainfall was recorded in October and November ( $234.4$  and  $117.9 \text{ mm m}^{-1}$ ,  
200 respectively). The average amount of rainfall increased significantly from  $7.4 \text{ mm m}^{-1}$  in

201 2005 (July-December), 70.9 mm m<sup>-1</sup> in 2006 (January-December) to 92.7 mm m<sup>-1</sup> in  
202 2007 (January-November).

203 The amount of water that infiltrates into caves depends on the types of soil and  
204 bedrock above the cave, the hydrology of the karst aquifer, and the water source (Atkinson,  
205 1977; Ford and Williams, 1989; Tooth and Fairchild, 2003; McDonald and Drysdale,  
206 2007). The drip rates at the OCNM range from no drip to continuous discharge at all sites  
207 except SR1 and SR2, where water flows throughout the year, and increase with the  
208 increase of the rainfall outside the cave (Fig. 2). At the other sites, there was no water  
209 discharge during much of the summer. After times of low or no rainfall, the water  
210 discharge in the cave usually starts a month after precipitation events. After heavy  
211 rainfall events the drip rates typically increases within 3-7 days. The drip rates were  
212 highest at the deepest sites (SR2 and SR1) and lowest at the shallowest site (IR) (Fig. 2b)  
213 but were not monotonically related to depth in the cave (KQR > MR).

#### 214 215 4.2. Chemical parameters and dripwater rates

216 The chemical analyses of the dripwater samples (pH, total alkalinity, calcium,  
217 magnesium, strontium, barium and sodium) are shown Figure 2. Obviously, the major  
218 and trace metal concentrations varied both seasonally and spatially (Fig. 2) where the  
219 highest concentrations were observed between November and December and deeper  
220 rooms with discrete drippings. For the purpose of understanding the similarity and  
221 dissimilarity among the different sites, the data set was statistically analyzed by cluster  
222 analysis; it was performed with the standardized data by Z score using Ward's method  
223 with squared Euclidean distances. The cluster analysis of the chemical parameters (Figure

224 3a) shows that only two groups were recognized; the first group included IR and KQR (<  
225 18 m depth) and the second group included MR, SR1 and SR2 (> 30 m depth). The  
226 depth of the site from surface and dripwater discharge also appears to affect calcium  
227 variability. Sites in the cave that are shallower (IR, KQR) or have slow drip rates (MR)  
228 show higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  variability than deep cave sites (SR1 and SR2). Slightly  
229 higher concentrations of calcium and magnesium are also detected when water discharges  
230 are slow at deeper drip sites.

231 The levels of the various measured parameters have been submitted to simple  
232 regression analyses to examine any probable correlation among them with emphasis on  
233 the dripwater rates for shallow and deep rooms. The correlations between the different  
234 physicochemical parameters of the shallow and deep rooms are shown in Table 1. For the  
235 shallower (<18m depth) site rooms such as the QQR and IR, the significant correlations  
236 are mainly for TA- $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ - $\text{Sr}^{2+}$  ( $p < 0.01$ ), where the dripwater rates are slow. The  
237 lack of significant correlations between other parameters such as TA- $\text{Mg}^{2+}$ , TA- $\text{Sr}^{2+}$ ,  
238  $\text{Mg}^{2+}$ - $\text{Ca}^{2+}$ ,  $\text{Ca}^{2+}$ - $\text{Sr}^{2+}$  is possibly due to incongruent dissolution and re-precipitation of  
239 calcium carbonate of different carbonate minerals. In deeper rooms (> 30 m depth) such  
240 as MR, SR1 and SR2, where the dripwater rates are discrete, the correlations are  
241 significant for Drip-pH, pH- $\text{Sr}^{2+}$ , TA- $\text{Ca}^{2+}$ , TA- $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ - $\text{Sr}^{2+}$  likely is caused  
242 mainly by congruent dissolution of carbonate bed rock. Obviously, dissolution process is  
243 the limiting factor that controls the concentrations of elements when the drip rates are  
244 continuous and fast. This indicates that residence time of percolated water in epikarst  
245 likely influences the concentration of elements in dripwaters.

246 Storage capacity and orientation of bedrock fractures influence the concentrations  
247 of major and trace elements in dripwaters (Tooth and Fairchild, 2003). Slow-moving  
248 ground waters require recharge threshold to reach different parts of the cave system. The  
249 major change in the water composition around November 2005 and 2006 is consistent  
250 with the increase in rainfall prior to these periods (September, 2005 and October, 2006).  
251 These concentration peaks are followed by decreases in these chemical parameters a  
252 month after November that persist throughout the rest of the rainy season.

253

#### 254 4.3. Processes controlling dripwater chemistry

255 Because of relatively high  $p\text{CO}_2$  derived from plant respiration and organic matter  
256 decay, dissolution processes are the main reactions in both the soil and epikarst zones  
257 (Hindy, 1971; Mayer, 1999). Therefore, dripwater solutions have geochemical  
258 information from rainfall, the soil component including organic matter and elements such  
259 as calcium, magnesium, strontium and phosphorous, and the mineralogy of the epikarst  
260 zone where dissolution and reprecipitation of calcium, magnesium, and strontium are  
261 expected.

262 To determine the possible sources of elements and physical and chemical  
263 processes that control the concentrations of the measured parameters, principle  
264 component analysis (PCA) was performed with the correlation coefficient matrix and the  
265 variance rotation with Kaiser Normalization. PCA analysis, with eigen value  $> 1.0$ ,  
266 identified two principle components for shallow and deeper rooms (Table 2). Factor  
267 loadings of  $> 0.75$  for variables were used for interpretation.

268 By treating the karst as one homogenous system and using all the data set to  
269 predict PC factors to physicochemical parameters, two principle components were  
270 extracted explaining 91.96% of the total variance. PC1 explains 78.62% of the variance,  
271 with pH, TA,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  as the predominant parameters (Fig. 3b). Thus,  
272 PC1 represents the major processes controlling the dripwater components, which are  
273 mainly dissolution of the bed rock, solid-solution reaction and water-rock ion exchange.  
274 A 13.34% of the variance is explained by PC2 showing a significant factor loading for  
275  $\text{Sr}^{2+}$ , likely dissolution of minerals containing strontium (e.g., crawfordite  
276 ( $\text{Na}_3\text{Sr}(\text{PO}_4)(\text{CO}_3)$ ), strontianite ( $\text{SrCO}_3$ ) and celestite ( $\text{SrSO}_3$ )).

277 The relationship between calcium and other elements can be used to investigate  
278 the dominant reactions and sources of these elements (Fairchild et al., 2000; McDonald et  
279 al., 2007; Cruz et al., 2007; Karmann et al., 2007). Table 2 shows the correlation between  
280 various elements and calcium concentrations in dripwater solutions. Both magnesium and  
281 strontium concentrations show significant positive correlations with calcium  
282 concentrations (Table 2) at the IR, SR1 and SR2 sites. This suggests that the main source  
283 of these elements (i.e., calcium, magnesium and strontium) is the dissolution of carbonate  
284 minerals in bedrock, which also confirmed by the results of PCA. These correlations are  
285 insignificant in the KQR and MR dripwater sites suggesting that the dissolution/re-  
286 precipitation reactions of carbonate minerals might not be the main sources of the major  
287 elements (i.e., Ca, Mg and Sr) in the solutions of these dripwater sites. Another  
288 explanation for this lower correlation is the dissolution of other minerals beside carbonate  
289 minerals such as calcium sulfate ( $\text{CaSO}_{4(s)}$ ). Sodium and barium show poor correlations

290 with calcium (Table 2), which suggest that the main source of these elements is the soil  
291 cover.

292 Since the dissolution and/or the precipitation of calcium carbonate ( $\text{CaCO}_{3(s)}$ )  
293 affects both total carbon dioxide and total alkalinity, the contribution of  $\text{CaCO}_{3(s)}$  can be  
294 confirmed by the correlation between TA calcium ion ( $\text{Ca}^{2+}$ ) concentrations. The  
295 correlations between TA and  $\text{Ca}^{2+}$  is significant at shallow and deep sites ( $r = 0.82-0.92$ )  
296 (Table 1), indicating that  $\text{CaCO}_{3(s)}$  is the major source of calcium ions. The number of  
297 moles of  $\text{CO}_3^{2-}$  that are involved in the formation of  $\text{CaCO}_{3(s)}$  or are released as a result of  
298  $\text{CaCO}_{3(s)}$  dissolution will change the carbonate alkalinity by a factor of 2 according to  
299 equation ( $\text{CA} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-})$ ). Thus, one would expect to obtain a slope of 2 by  
300 plotting CA against  $\text{Ca}^{2+}$  if the main cause of the CA change is the dissolution or  
301 precipitation of  $\text{CaCO}_{3(s)}$ . The estimated slopes are respectively 1.91, 1.98 and 1.96 and  
302 1.67 ( $1.88 \pm 0.14$ ) for the IR, MR, SR1 and SR2 sites (Fig. 4b), confirming that  $\text{CaCO}_{3(s)}$   
303 bedrock is the main source of Ca, Mg, and Sr in IR, MR and SR sites. This is also  
304 supported by the significant correlations between Mg-Ca and Sr-Ca for SR1 and SR2  
305 (Table 2). The slope of 1.07 for the KQR site suggests that additional minerals are  
306 involved in the contribution of Ca concentration in dripwater. One of these minerals is  
307 likely to be  $\text{CaSO}_{4(s)}$ , which will increase the concentration of calcium ion relative to  
308 carbonate alkalinity and eventually reduce the slope.

309

#### 310 4.4. The saturation levels of dripwater solutions with respect to carbonate minerals

311 Values of  $\% \Omega$  were estimated for pure calcite, aragonite, and vaterite minerals.  
312 All sites showed that the dripwaters were supersaturated with respect to pure calcite and



313 aragonite and undersaturated with respect to vaterite (Table 4; Fig. 5). They ranged from  
314 86% to 528% (mean =  $262 \pm 111$ ), 59% to 368% (mean =  $182 \pm 77$ ), and 21% to 128%  
315 (mean =  $63 \pm 26$ ) for calcite, aragonite and vaterite, respectively.

316 The degree of saturation of the dripwater is an important parameter to assess its  
317 chemistry and the tendency for stalagmite formation or dissolution. At the KQR and MR  
318 sites, the dripwaters were saturated to supersaturated with respect to pure calcite and  
319 aragonite and undersaturated to supersaturated at IR SR1 and SR2 sites. All sites are  
320 undersaturated to saturated with respect to vaterite. We also note that the degree of  
321 saturation generally increases with the decreases of drip rates in May-June 2006 and 2007,  
322 when solutions become more supersaturated when the drip rate is slow (Figs 2 and 5).

323 Various natural waters (i.e., spring, ground, oceanic and pore waters) are often  
324 found to be supersaturated with respect to both calcite and aragonite, but without  
325 inorganic precipitation of  $\text{CaCO}_{3(s)}$  (Weyle, 1961; Pytkowicz, 1965; Berner, 1975). It is  
326 well established that the magnesium content of calcite has a direct effect on the physical  
327 and chemical behavior of  $\text{CaCO}_{3(s)}$  and its solubility (Chave et al., 1962; Bischoff and  
328 Fyfe, 1968; Lahann, 1978a,b; Mackenzie et al., 1982; Mucci and Morse, 1984; Mucci et  
329 al., 1985; Rushdi, 1995; Rushdi et al., 1992, 1998). Chave et al. (1962) showed that the  
330 solubility of calcium carbonate increases in the order of pure calcite, low magnesian  
331 calcite, aragonite and high magnesian calcite. Previous studies have shown that the  
332 solubility of magnesian calcite increases by the increase of Mg content of  $\text{CaCO}_{3(s)}$   
333 (Plummer and Mckenzie, 1974; Thorstenson and Plummer, 1977; Land, 1967; Chave et  
334 al., 1962, Walter and Morse, 1984; Mucci and Morse, 1984; Rushdi et al., 1992, 1998).  
335 This may produce dripwater solutions with high Mg concentrations and supersaturated

336 with respect to pure calcite. The maximum super saturation range where low magnesian  
337 calcite may form is about 528% (Rushdi et al., 1998). However, the dripwater solutions  
338 are supersaturated with respect to pure calcite and aragonite, so they are likely to be  
339 undersaturated with respect to high magnesian calcite. Therefore, one would expect that  
340 pure and low magnesian calcite will form as a speleothem deposit.

341

#### 342 4.5. Mg/Ca and Sr/Ca ratios of dripwaters

343 Prolonged interaction between groundwater and bedrock enhances dissolution of  
344 calcium carbonate bedrock increasing the saturation levels of calcium carbonate and the  
345 concentrations of Ca, Mg, Sr and other trace metals in solution. The dripwaters in caves  
346 are expected to have a high degree of saturation (i.e., high Ca concentration) (Fig. 6a)  
347 with respect to calcium carbonate minerals. Different Mg/Ca and Sr/Ca ratios due to  
348 enhanced dissolution of various carbonate minerals and possible calcite reprecipitation  
349 are expected (Fairchild et al. 2000; Day and Henderson, 2013). We find that shallow sites  
350 show relatively high concentrations of Ca and lower degree of superaturation, whereas  
351 deeper sites show lower Ca concentrations and higher degree of super saturation (Fig. 6a).  
352 This is likely due to longer contact times of waters and bedrock and reprecipitation of  
353 low magnesian calcite in deeper sites.

354 The Mg/Ca and Sr/Ca ratios fluctuate at slow and fast drip sites (Figs. 2b) and the  
355 values of Ca, Mg and Sr concentrations (Fig. 2) also suggest that the bedrock (with  
356 different calcium carbonate minerals) is the main factor that influences the chemistry of  
357 the dripwaters in the cave. The results also show that there is an increase in the Sr/Ca  
358 with the increase of Mg/Ca (Fig. 6b). Shallow sites (e.g. IR) show low values of both

359 Mg/Ca and Sr/Ca ratios with no obvious trend. This is likely due to reprecipitation of  
360 magnesian calcite on the surfaces of bedrock fractures. This is supported by the low  
361 Mg/Ca ratios and relatively lower degree of saturation at shallow sites (IR and KQR)  
362 relative to the high ratios and higher saturation levels with respect to calcium carbonate in  
363 deeper sites (SR1 and SR2) (Fig. 6).

364 Dilution effects are likely to be insignificant in these dripwater sites; therefore, Ca  
365 variation relative to Mg/Ca and Sr/Ca in dripwaters is likely controlled by dissolution of  
366 different  $\text{CaCO}_{3(s)}$  minerals (e.g., calcite with different mole percent Mg, aragonite, and  
367 dolomite) and calcite reprecipitation in the routes and cracks above the cave. Calcite  
368 reprecipitation apparently increases in dry seasons because air circulation increases in the  
369 epikarst as a result of low level of ground waters of high degree of saturation with respect  
370 to calcium carbonate (Fairchild et al., 2000; Tooth and Fairchild, 2003; Musgrove and  
371 Banner, 2004; McDonald et al., 2004; Fairchild et al., 2006; Day and Henderson, 2013).  
372 This will increase the relative co-precipitation of Mg and Sr and decrease the Mg/Ca and  
373 Sr/Ca ratios in dripping waters of shallow sites (Fig. 6c and d). During the wet season,  
374 when the degree of supersaturation is expected to be comparatively lower, low magnesian  
375 calcite precipitates and less Mg and Sr are co-precipitated in the mineral phase leading to  
376 high dripwater Mg/Ca and Sr/Ca ratios. Sr/Ca ratios show slightly different behavior due  
377 to likely different bedrock carbonate minerals as is explained below.

378 These observations suggest that the degree of supersaturation of the solution and  
379 rate of calcite reprecipitation, which differ seasonally, control the variations of Mg/Ca  
380 and Sr/Ca ratios in dripwater solutions. This is because the partition coefficients of Mg  
381 and Sr are less than 1 in dilute solutions (Mucci and Morse, 1983; Morse and Bender,

382 1990; Huang and Fairchild, 2001). In addition, the ionic sizes of Ca (radius = 112 pm),  
383 Mg (radius = 86 pm) and Sr (radius = 132 pm) have differing effects on the chemical and  
384 physical behaviors of the carbonate minerals. Sr is more commonly associated with  
385 aragonite and is found to increase the solubility of aragonite, while Mg is associated with  
386 calcite and increases its solubility (Chave et al., 1962; Land, 1967; Plummer and  
387 MacKenzie, 1974; Mucci and Morse, 1984; White, 1994, 2004). Usually, the Sr/Ca ratio  
388 in aragonite is higher than in calcite, so that the dissolution and transformation of  
389 aragonite to calcite releases Sr into the solution (Huang et al., 2001; Fairchild and  
390 Killawee, 1995; White, 2004; McMillan et al., 2005). This indicates that the increase in  
391 Sr/Ca ratios in KQR is likely attributed to the presence of aragonite in the bedrock.

392 The exponential decrease of Ca in solution relative to both Mg/Ca and Sr/Ca  
393 ratios in these dripwaters (Fig. 6e and f) suggests that calcite reprecipitation, which is  
394 clearly shown in shallow sites, can be considered as the key chemical reaction that  
395 controls the variation in elemental ratios in dripwater of the OCNM cave system.  
396 Therefore, trace metals in speleothem deposits at the OCNM can be used as  
397 paleoclimatological proxies for precipitation, if interpreted within the context of  
398 understanding local bedrock chemistry.

399

400

## 401 **5. Conclusions and paleoclimate implications**

402 Dissolution and reprecipitation are likely the main processes that control the  
403 chemistry of the dripwaters in the OCNM cave system. Calcite reprecipitation could be a  
404 key process at parts of the epikarst and causes homogenous short-term variation in major

405 and trace elements in dripwaters in the system. Seasons with low rainfall are associated  
406 with increases in Ca, Mg, and Sr concentrations karst solutions. This is followed by  
407 relative increases in Mg/Ca and Sr/Ca concentration ratios relative to the concentration of  
408 Ca in the dripwaters due to re-precipitation of calcite along flow routes.

409 Spatiotemporal covariance of chemical parameter suggests that stalagmites in this  
410 cave might record the major and trace metal variations as a result of changes in  
411 hydrological conditions. In particular, Mg/Ca and Sr/Ca in speleothems from OCNM  
412 may serve as proxies of past climate. The spatial chemical variations in the OCNM cave  
413 waters are apparently influenced by the mineralogy of the bedrock and the flow routes,  
414 which cause the differences in their values and the slopes of Mg/Ca and Sr/Ca ratio  
415 trends. This suggests that Mg/Ca and Sr/Ca at a given location in the ONCM cave system  
416 can be used as qualitative proxies for seasonal changes of past rainfall as long as  
417 groundwater pathways to each site remain constant, but that quantitative interpretations,  
418 or combination of data from multiple sites, would require site-specific calibration.

419

420

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424

425

426 **References**

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- 636

**Table 1.** Spearman correlation coefficient (r) of physicochemical parameters of drip-water samples from shallow (< 18m) and deep (> 20m) rooms at Oregon Caves National Monument from 2006-2007.

Shallow Rooms (KQR & IR)								
Drip	pH	TA	Ba2+	Ca2+	Mg2+	Na+	Sr2+	
Drip	1	-0.014	-.402*	0.126	-.370*	-0.121	-0.214	-0.061
pH		1	-0.058	.409*	-0.258	-0.035	-0.14	0.063
TA			1	-.362*	.924**	0.271	0.007	0.183
Ba2+				1	-.407*	.351*	0.157	.439*
Ca2+					1	0.252	0.093	0.151
Mg2+						1	0.175	.940**
Na+							1	0.136
Sr2+								1
Mg/Ca								
Sr/Ca								
Ba/Ca								
Na/Ca								
Deep Rooms (MR & SR1+2)								
Drip	1	.546**	-.313*	0.21	-0.202	.356*	-.281*	-.287*
pH		1	-0.253	.293*	-0.177	-0.015	-0.162	-.387**
TA			1	-0.273	.818**	0.086	-0.028	.431*
Ba2+				1	-.454*	-0.018	0.035	0.052
Ca2+					1	0.188	-0.034	.396*
Mg2+						1	0.13	.600**
Na+							1	0.251
Sr2+								1
Mg/Ca								
Sr/Ca								
Ba/Ca								



**Na/Ca**

\*\* Correlation is significant at the 0.01 level (2-tailed); \* Correlation is significant at the 0.05 level (2-tailed).

ACCEPTED MANUSCRIPT

**Table 2.** Principal component (PC) factors to physicochemical parameters of dripwaters from all cave sites.

	All	
	PC1	PC2
Dripping	0.701	-0.229
pH	0.976	-0.198
TA	-0.944	0.323
Ba <sup>2+</sup>	0.974	0.089
Ca <sup>2+</sup>	-0.923	0.345
Mg <sup>2+</sup>	0.947	-0.294
Na <sup>+</sup>	0.757	-0.605
Sr <sup>2+</sup>	-0.119	0.98
Eigen value	6.29	1.068
Total variance (%)	78.62	13.34
Cumulative (%)	78.62	91.96

**Table 4.** Carbonate chemical parameters of dripwater solutions from Oregon Caves

National Monument Cave.

	<b>Site</b>				
	<b>IR</b>	<b>KQR</b>	<b>MR</b>	<b>SR1</b>	<b>SR2</b>
<b>Sampling Period</b>	Jan 05-Apr 07	Dec 05-May 07	Dec 06-May07	Jan-Jul 2007	Dec 06-Jul 08
<b>CA (meq L<sup>-1</sup>)</b>					
Minimum	2.1015	2.1408	1.9989	2.0778	2.1314
Maximum	2.9200	2.8134	2.6539	2.3812	2.3316
Mean (Standard Deviation)	2.4710 (0.2200)	2.4407 (0.0616)	2.2997 (0.0444)	2.2047 (0.0228)	2.1891 (0.0611)
<b>TCO<sub>2</sub> (mole L<sup>-1</sup>)</b>					
Minimum	2.1459	2.1637	2.0197	2.0806	2.1245
Maximum	2.9657	2.8266	2.6620	2.4434	2.3701
Mean (Standard Deviation)	2.5043 (0.2231)	2.4683 (0.0633)	2.3165 (0.0431)	2.2220 (0.0285)	2.2030 (0.0777)
<b>%Ω (Calcite)</b>					
Minimum	86	151	156	139	131
Maximum	528	462	472	375	396
Mean (Standard Deviation)	262 (110)	267 (22)	277 (20)	279 (25)	284 (85)
<b>%Ω (Aragonite)</b>					
Minimum	59	105	108	97	91
Maximum	368	322	328	261	275
Mean (Standard Deviation)	182 (77)	186 (15)	193 (14)	194 (17)	197 (59)
<b>%Ω (Vaterite)</b>					
Minimum	21	36	38	34	32
Maximum	128	112	114	91	96
Mean (Standard Deviation)	63 (26)	64 (5)	67 (5)	67 (6)	69 (21)

**Figure Captions**

**Figure 1.** Map showing the locations of (a) Oregon Caves National Monument (OCNM), which is located in the Klamath Mountains, western the United States of America and (b) the water sampling sites in the OCNM caves.

**Figure 2.** Monthly variations of: (a) Rainfall, (b) dripwater rate, (c) pH, (d) total alkalinity (TA), (e) calcium ( $\text{Ca}^{2+}$ ), (f) magnesium ( $\text{Mg}^{2+}$ ), (g) strontium ( $\text{Sr}^{2+}$ ) and (h) barium ( $\text{Ba}^{2+}$ ) in dripwaters during monitoring program from January 2005 to April 2007.

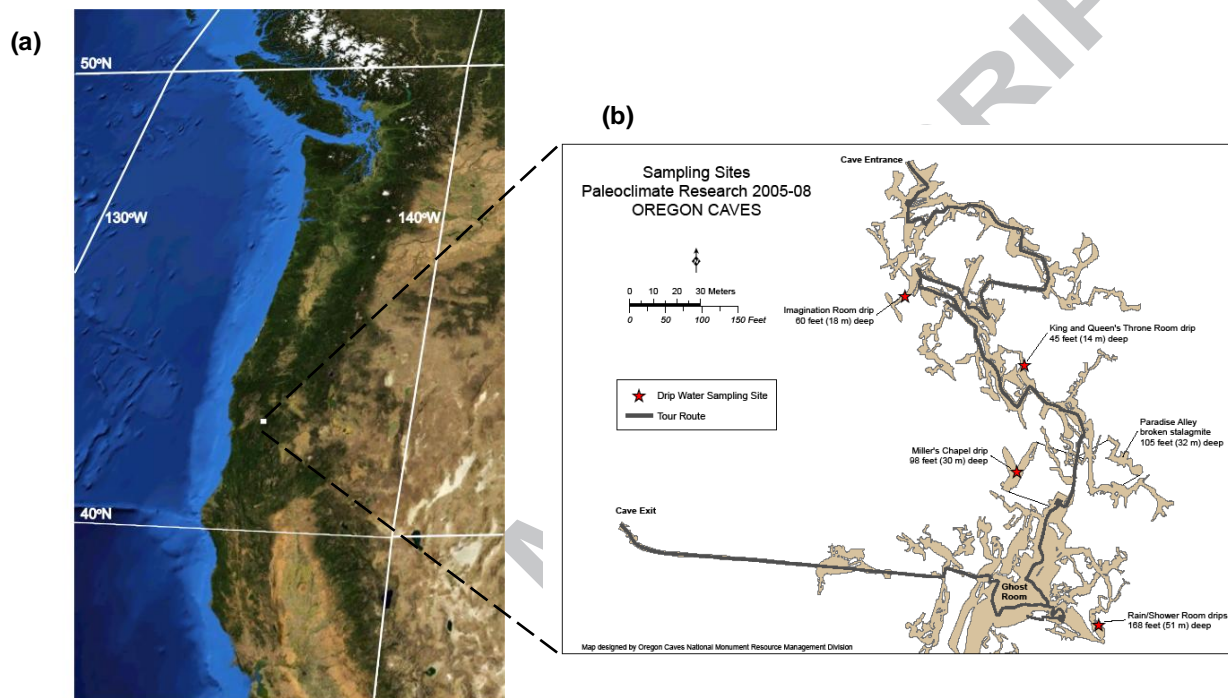
**Figure 3.** Plot showing: (a) the dendrogram of cluster analysis (CA) and (b) the principal component analysis (PCA) for the physicochemical parameters.

**Figure 4.** Plots of Carbonate alkalinity (CA) vs. calcium ( $\text{Ca}^{2+}$ ) for dripwaters of all sites.

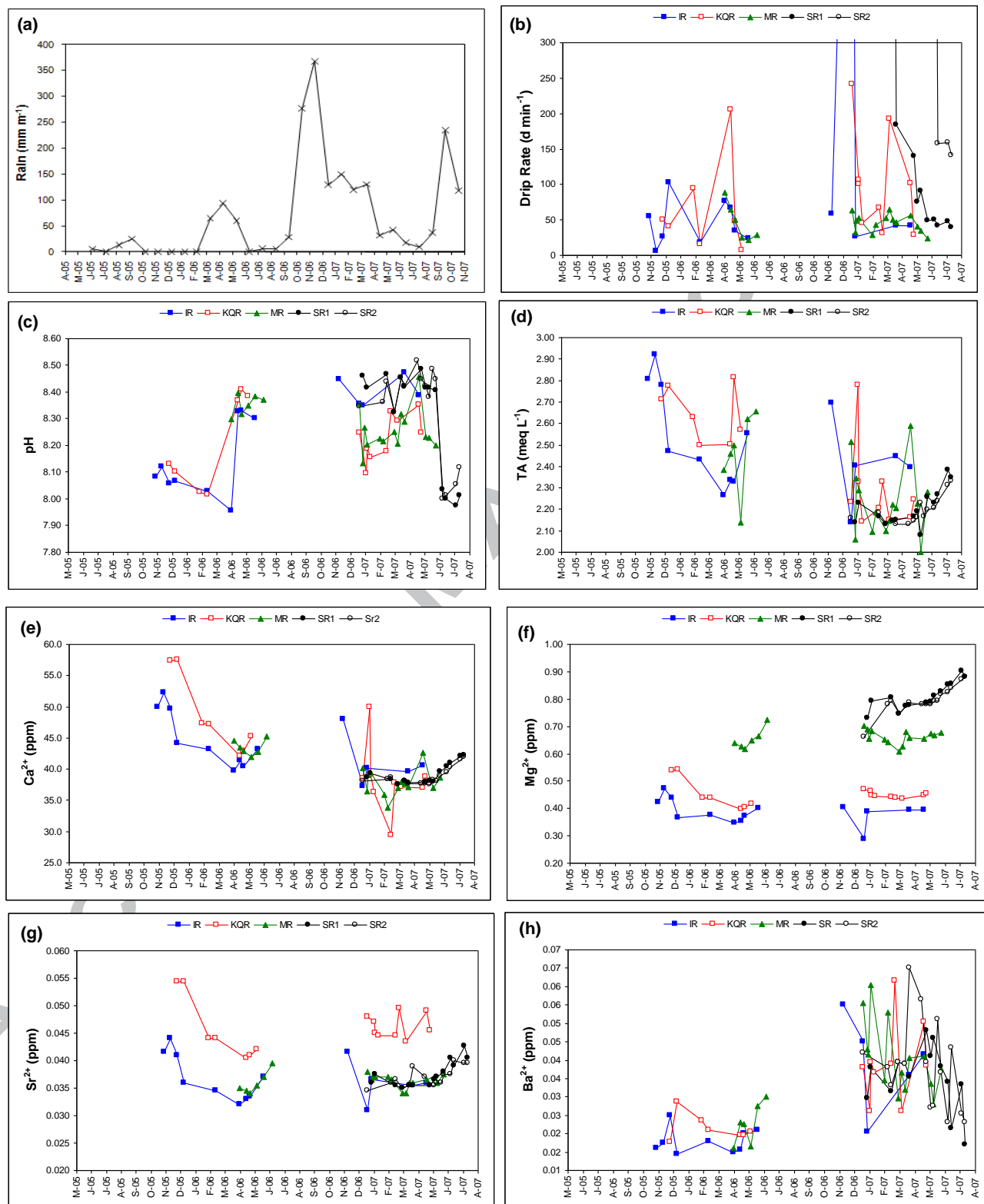
**Figure 5.** Percent saturations of the drip waters with respect to: (a) calcite, (b) aragonite and (c) vaterite.

**Figure 6.** Plots of the variation trends and relationships between different parameters in dripwaters of the different rooms as a result of dissolution and reprecipitation reactions: (a) Ca vs.  $\Omega\%$ , (b) Sr/Ca vs Mg/Ca ratios, (c)  $\Omega\%$  vs. Mg/Ca ratios, (d)  $\Omega\%$  vs. Sr/Ca ratios, (e) Ca vs. Mg/Ca ratio, and (f) Ca vs. Sr/Ca ratio for all sites.

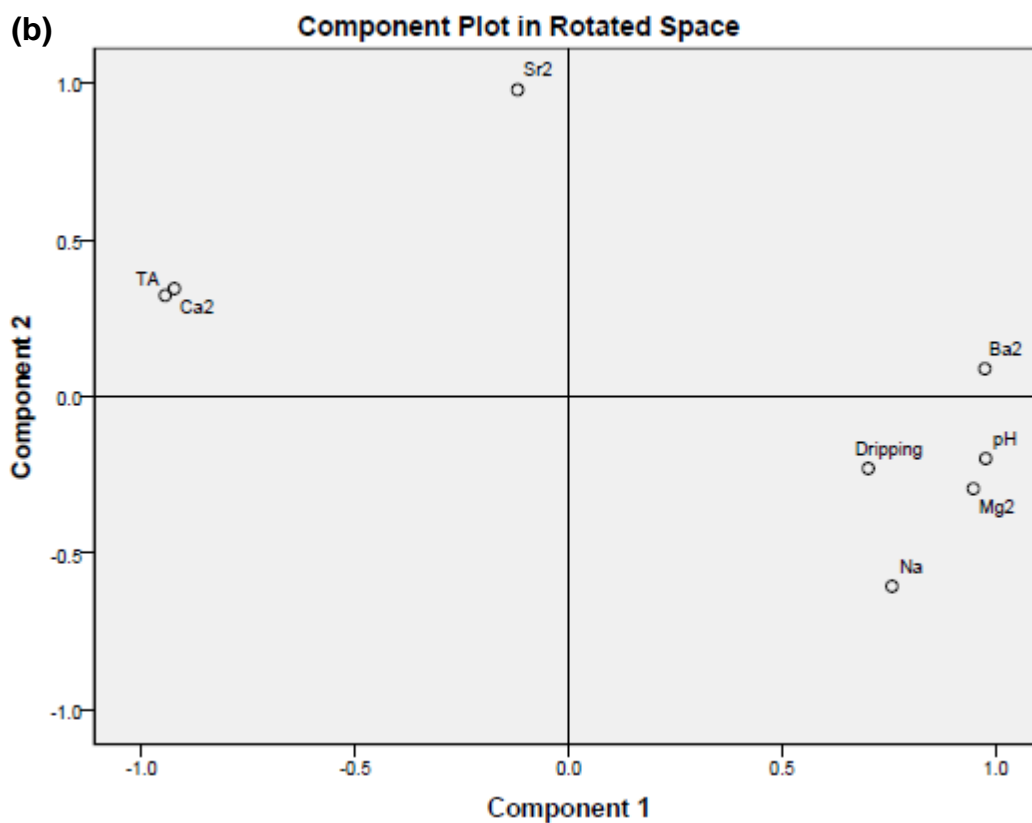
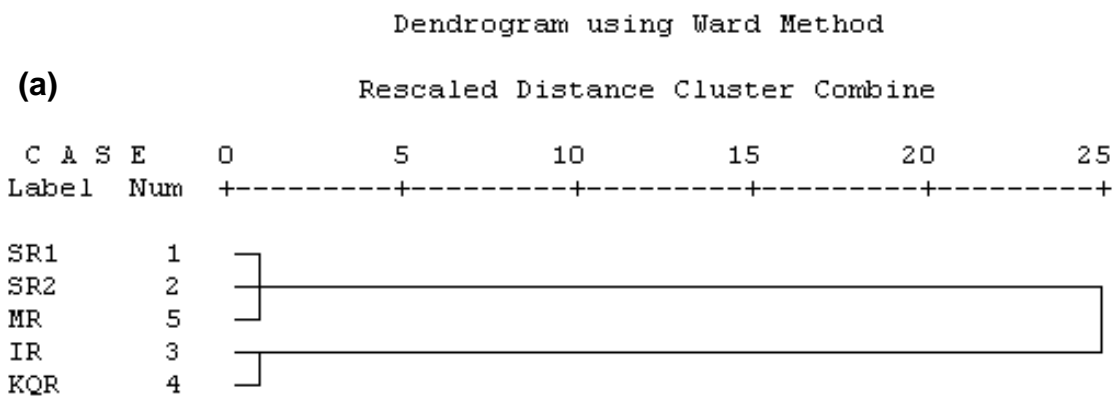
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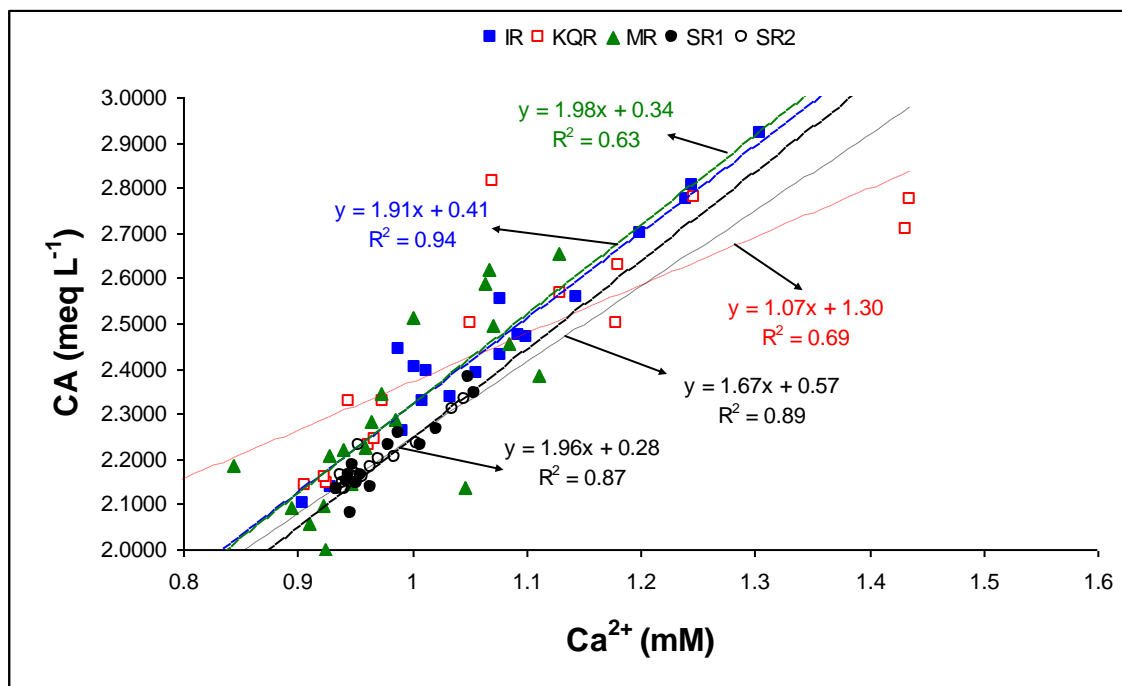
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F3



F4





F5

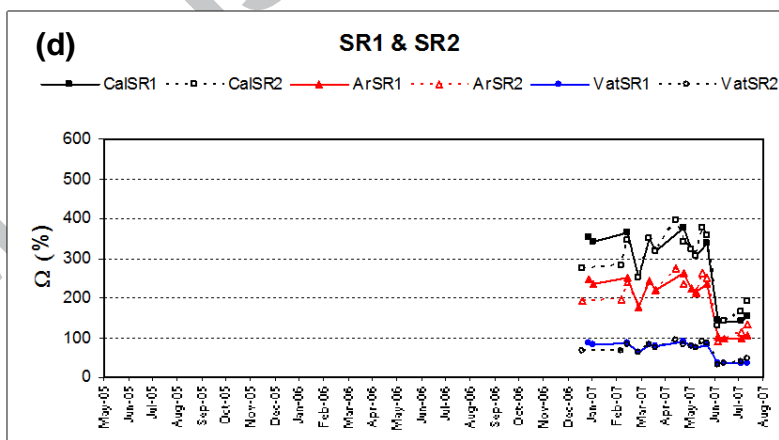
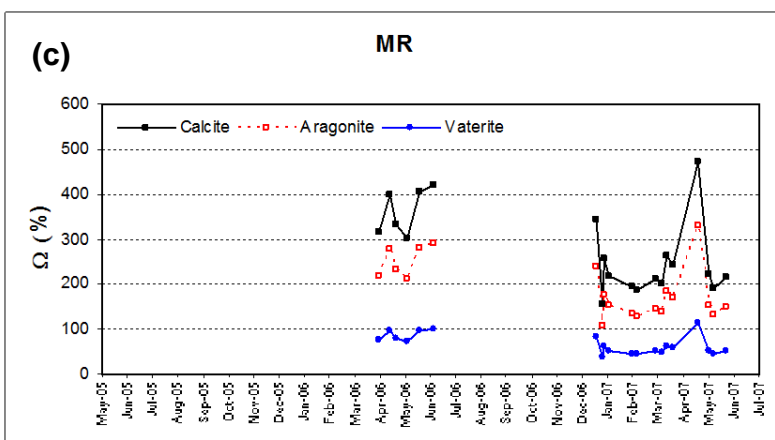
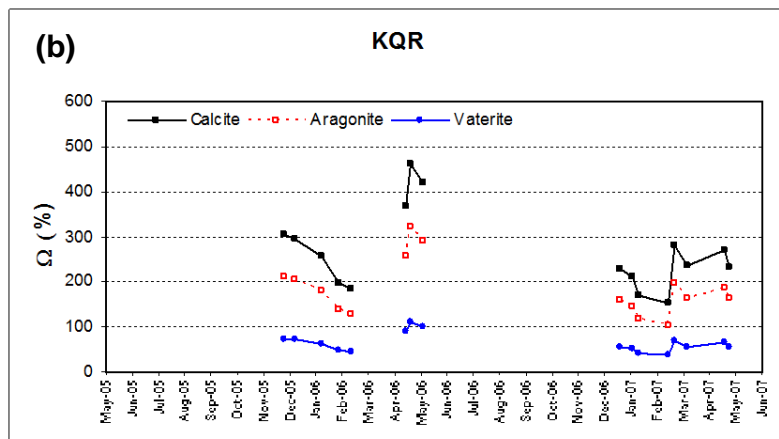
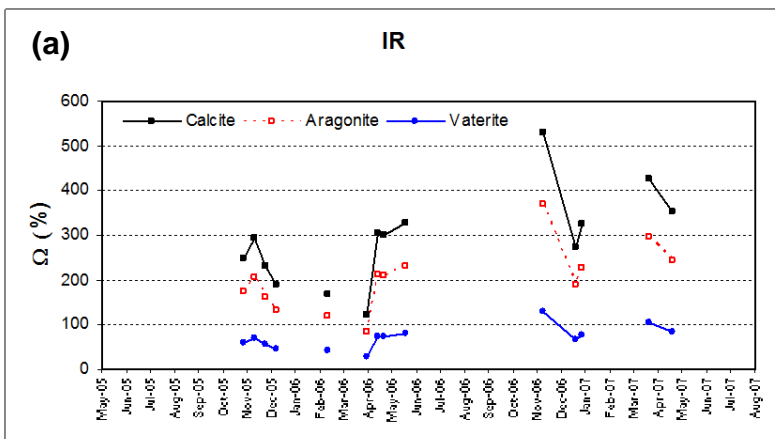
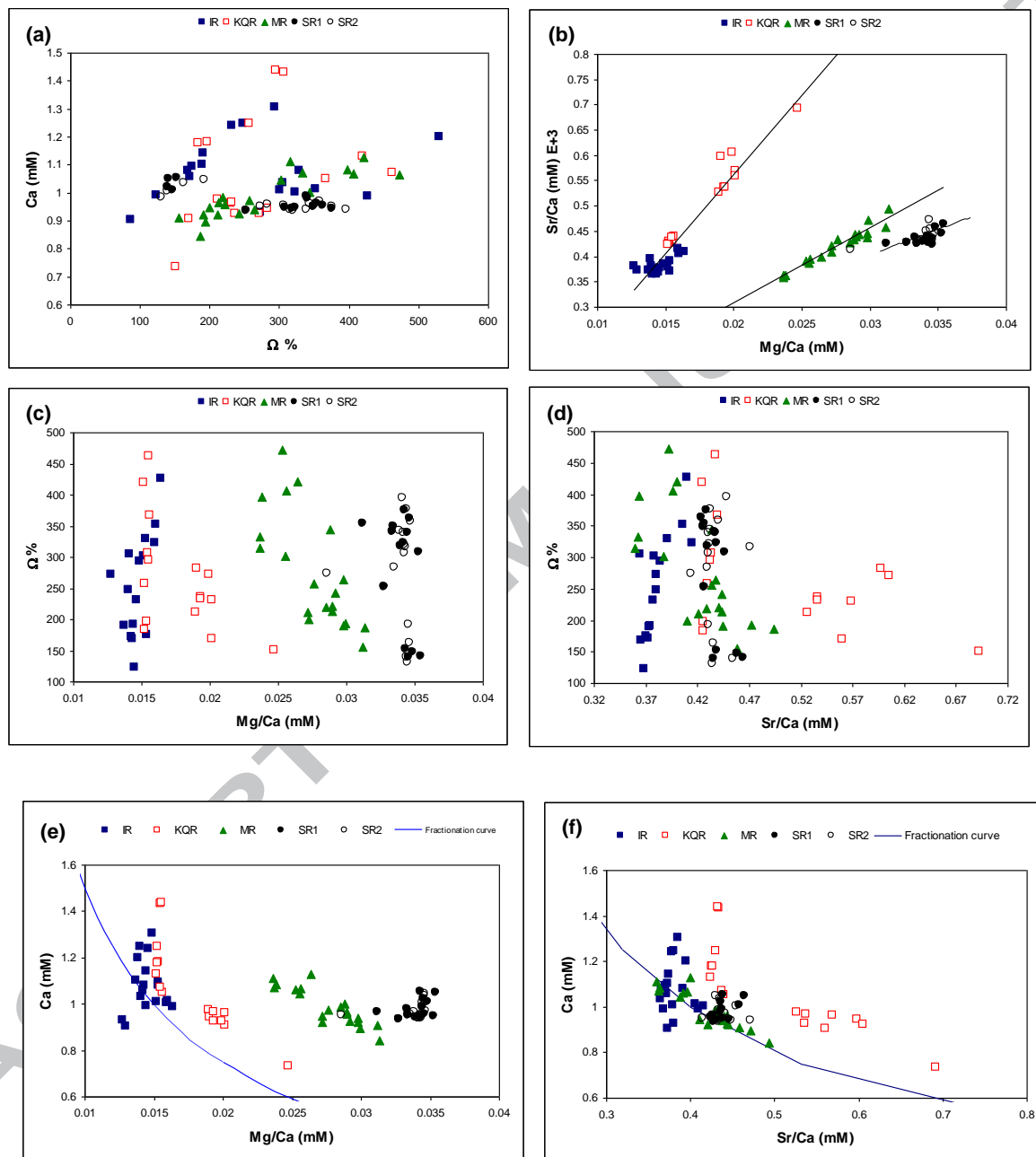


Fig 6



**Highlights**

- Cave dripwater chemistry of Oregon Caves National Monument (OCNM) was studied.
- The dripwater varies in response to seasonal changes in rainfall.
- Spatial variations of dripwater chemistry reflect the chemical composition of bedrock
- The residence time of infiltrated water in bedrock cracks control the dissolution and reprecipitation of calcium carbonate.
- Dripwater Mg/Ca and Sr/Ca ratios are controlled by dissolution and reprecipitation of carbonate bedrock.