1	Large–scale stable isotope alteration around the
2	hydrothermal carbonate-replacement Cinco de Mayo
3	Zn-Ag deposit, Mexico
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#### ABSTRACT

Carbonate-hosted hydrothermal deposits typically show narrow visible mineralogical and 31 textural alteration halos, which inhibits exploration targeting. In contrast, hydrothermal 32 33 modification of the country rock's stable isotope composition usually extends far beyond the limited visible alteration. Hence, stable isotope studies should be an effective tool to aid 34 exploration for carbonate-hosted deposits. Here we present new insight into the development of 35 36 a large stable isotope alteration halo based on 910 O and C isotope analyses of carbonate veins 37 and hydrothermally altered limestone hosting the Cinco de Mayo Pb-Zn-Ag (Au, Cu) Carbonate Replacement Deposit (CRD), in Chihuahua, Mexico. Our results demonstrate that stable isotope 38 alteration is consistent with reactive, magmatic fluid flow into unaltered limestone and represents 39 a powerful tool for the characterization of these hydrothermal ore systems. Syn-mineralization 40 veins are texturally and isotopically distinct from those formed during pre- and post-41 mineralization diagenesis and fluid flow and show distinct gradients along the direction of 42 mineralizing fluid flow: this appears to be a promising exploration vectoring tool. Downhole 43 variations in wall rock isotope values reveal aquifers and aquicludes and outline the principal 44 hydrothermal flow paths. Furthermore, wall rock  $\delta^{18}O_{VSMOW}$  systematically decreases towards 45 46 mineralization from  $\sim 23\%$  to < 17% over a distance of  $\sim 10$  km, providing another vectoring tool. The extent of the stable isotope alteration halo likely reflects the overall fluid volume and areal 47 extent of a fossil hydrothermal system, which may be expected to scale with the mineral 48 endowment. This suggests that constraining the size, shape and degree of isotopic alteration has 49 direct application to mineral exploration by outlining the system and indicating the potential size 50 of a deposit. 51

#### **INTRODUCTION**

54 The stable isotope compositions of natural fluids and rocks are generally different, so mineral replacement reactions occurring during hydrothermal rock alteration often result in 55 distinctly modified isotope ratios ( $\delta^{18}$ O,  $\delta^{13}$ C) of the affected rock relative to its precursor 56 57 (Cathles, 1993; Taylor, 1974, 1979; Taylor and Epstein, 1963). Hydrothermal ore deposit formation involves large volumes of disequilibrium fluids that interact with the country rock 58 causing halos of isotopic alteration (e.g.  $\delta^{18}$ O and  $\delta^{13}$ C) showing values distinct from more distal, 59 unaltered rocks. These disequilibrium fluids also commonly deposit secondary carbonate veins 60 with distinct isotopic values. The spatial extent of isotopic alteration and isotopically distinctive 61 carbonate veins usually extends far beyond zones of visible alteration and metal enrichment (e.g. 62 Criss et al., 1985). Therefore, stable isotope mapping represents a potentially powerful 63 prospecting tool complementing other mineral exploration techniques (e.g., mineralogy, 64 lithogeochemistry, geophysics). 65

The extent and degree of isotopic alteration of a given host rock depends on the fluid 66 transport mode (pervasive or channelized), fluid and rock composition, fluid volume and 67 temperature dependent reaction kinetics (e.g., Frimmel, 1992; Lassey and Blattner, 1988). The 68 69 utilization of stable isotope studies in exploration for hydrothermal ore deposits in carbonate rocks is particularly attractive because they typically develop very limited visible alteration zones 70 immediately around fluid flow paths (see also Criss et al., 2000; Ewers et al., 1994; Kelley et al., 71 2006; Large et al., 2001; Taylor, 1997; Vazquez et al., 1998; Waring et al., 1998). Even though 72 73 stable isotope studies can yield critical constraints on fluid composition and source, alteration 74 temperature and size of the hydrothermal system, their practical application is surprisingly limited to only one successful documented discovery (Naito et al., 1995). Historically, the main 75 reasons for the limited practical deployment of stable isotope mapping in mineral exploration 76 77 were unacceptably high costs of data collection and long turn-around times. Consequently, stable 78 isotope studies of hydrothermally altered country rocks have been limited to purely academic research despite the potential for improving mineral exploration in some environments (Barker et 79 al., 2013; Dilles et al., 1992; Hickey et al., 2014; Jamtveit et al., 1992; Millonig et al., 2017; 80 81 Murakami and Nakano, 1999).

This study aims to further understanding of how the stable isotope compositions of 82 hydrothermally altered limestone can be used as a vectoring tool in carbonate replacement 83 deposits through use of an off-axis integrated cavity output spectrometer that allows for high 84 sample throughput at minimal analytical cost (OA-ICOS) (Barker et al., 2011; Barker et al., 85 2013; Beinlich et al., 2017). Vein and wall rock carbonate samples (n = 910) from 16 drill holes 86 around the Cinco de Mayo Pegaso Zone mineralization were examined and analyzed for textural 87 characteristics and isotope and trace-element compositions to define the overall extent of the 88 89 stable isotope alteration footprint, identify fluid and metal transport pathways, and to assess the transitions in stable isotope signatures from proximal intrusion-related skarn to distal carbonate 90

hosted manto systems. The results provide new constraints on the volume of alteration fluids,
their composition and source, and the critical dimensions of fluid transport in a large
hydrothermal system.

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#### **GEOLOGICAL CONTEXT**

#### 95 *General overview*

96 The Cinco de Mayo Zn-Ag carbonate replacement deposit (CRD) is located in the State of Chihuahua, Mexico approximately ~190 km north of the capital, Chihuahua City (Robertson and 97 Megaw, 2009). Cinco de Mayo is one of a family of CRDs that define a belt 2200 km long along 98 the interface between the Tertiary Volcanic Plateau of the Sierra Nevada Occidental and the 99 Laramide Mexican Thrust Belt (Megaw et al., 1988). The most significant CRDs are hosted in 100 101 carbonate successions of the Chihuahua and Sierra Madre terranes, which together with the Coahuila and Maya terranes are underlain by Paleozoic or possibly older continental crust (Ruiz 102 et al., 1988). Mineralization throughout the belt occurs in a limestone-dominant transgressive 103 sedimentary succession deposited during Jurassic-Cretaceous flooding of pre-Middle-Triassic 104 basement terranes (Haenggi, 2002). This basement was block-faulted during middle-Jurassic 105 extension, creating a series of linear basins, including the Chihuahua Trough that controlled 106 sedimentation (Megaw et al., 1996). The deposit is situated at the western boundary of the 107 Chihuahua Trough where thrust sheets of Cretaceous limestone, shale, and sandstone were 108 109 stacked by basin inversion during NE-SW directed Laramide compression between ~84 Ma and ~43 Ma (Muehlberger, 1993). This NE-SW compression was accompanied by gentle to tight 110 folding and extensive axial faulting and fracturing (Handschy and Dyer, 1987; Hewitt, 1966) that 111 created structurally enhanced permeability subsequently exploited by mid-Tertiary intrusions 112 ranging in composition from diorite through rhyolite. Hydrothermal fluids related to these 113 114 magmas also followed these deformation zones; depositing a range of skarn, CRD and vein deposits (Clark and de la Fuente L, 1978; Megaw et al., 1988). Megaw et al. (1988) noted that 115 mineralization is commonly hosted in limestone layers capped by impermeable strata that 116 confined fluid flow and mineral precipitation to distinct zones. Lead isotope data from mineral 117 118 deposits in northern Mexico suggest substantial reworking of Pb from underlying Precambrian crust during Cenozoic volcanism linked to rapid spreading at the East Pacific Rise prior to the 119 opening of the Gulf of California (Cumming et al., 1979; McDowell and Keizer, 1977; Nieto-120 Samaniego et al., 1999). The timing of mineralization throughout the region is bracketed between 121 57.9 Ma and 25.9 Ma, coinciding with the main period of the Tertiary Sierra Madre Occidental 122 volcanic activity, with maxima between 35 Ma and 29 Ma (Camprubi et al., 2006; Megaw et al., 123 1988; Velador et al., 2010). 124

#### 125 The Cinco de Mayo Carbonate Replacement Deposit

126 Cinco de Mayo is a recently discovered Ag–Pb–Zn carbonate replacement deposit within a 127 25,000 hectare concession 100% owned by MAG Silver Corp. The property is centered on the

Sierra Santa Lucia, a 4 km wide, 15 km long ridge composed of imbricated thrust sheets of 128 limestone, sandstone and shale. The sierra is surrounded by a flat, featureless alluvial plain that 129 stretches for several kilometers in all directions. This plain is interrupted on its east side by a 130 0.5×2.0 km long elongated limestone ridge (Cerro Cinco de Mayo) cut by numerous mineralized 131 132 jasperoid veins (Robertson and Megaw, 2009). Exploration began in 2006 along this ridge and 133 rapidly progressed into the surrounding covered areas guided by repeated iterations of geological interpretation, airborne geophysical surveys and drilling. This ultimately defined mineralization 134 in imbricated slices of limestone along the NW-trending Jose Thrust Fault. Concurrent 135 136 exploration through the alluvial cover about 4 km to the SW along the west side of the Sierra Santa Lucia discovered the Pozo Seco Zone mineralization in 2008. The Pozo Seco Zone also 137 lies directly along a major thrust fault and consists of a tabular jasperoid body, ~2.5 km long, 250 138 to 300 m wide, and 17 to 250 m thick, carrying average grades of 0.15% Mo and 0.25 ppm Au 139 140 (MacInnis, 2009, 2010).

Initial drilling at Cinco de Mayo Ridge in 2007 intersected minor massive sulfides plus 141 massive hornfels alteration cut by dispersed and veinlet Zn-Pb sulfide mineralization (Robertson 142 and Megaw, 2009). Continued drilling between 2007 and 2012 discovered and defined the 143 144 "Upper Manto", a continuous body of massive sulfides averaging 5 m thick, 450 m down dip and 4,000 m long. In mid-2012 drill hole CM12-431, directed beneath the centre of the Upper 145 Manto, encountered the Pegaso Zone comprised of three major massive sulfide zones (3.12 m, 146 20.15 m and 61.6 m in core length) lying within a zone of pervasive skarn and marble 147 approximately 400 m thick. The thickest intercept (61.1 m) graded 89 g/t silver, 0.78 g/t gold, 148 0.13% copper, 2.1% lead and 7.3% zinc (MacInnis, 2012). Despite the pervasive skarn and 149 marble development, no intrusions were cut in the hole. The entire progression of continuous 150 mineralization from the Upper Manto to the Pegaso Zone is completely blind, with no outcrop 151 152 expression whatsoever.

The known mineralization is hosted within fossiliferous limestone of the Lower Cretaceous 153 Finlay Formation along NE-SW and NW-SE trending structures, dominantly where faulted 154 against impermeable shales and sandstones of the Upper Cretaceous Benavides Formation 155 156 (Lyons, 2008). Mineralization occurs as relatively flat lying to inclined sheet-like massive sulfide "manto" (Spanish for "cloak" or "blanket") replacement bodies in the limestone with 157 sulfide mineralized veinlets in the hanging wall shales and sandstones. Mantos consist of massive 158 fine to coarse-grained pyrite, pyrrhotite, galena, sphalerite, with minor chalcopyrite and 159 acanthite. Domains of unreplaced limestone are common within the massive sulfides. Common 160 gangue minerals include barite, fluorite, and manganoan calcite (Megaw et al., 2014). Coarse-161 grained sulfide-mineralized veinlets dominated by Mn-calcite occur along vein walls, in calcite-162 cemented breccia, and as stringers replacing the vein calcite. Sulfide minerals are commonly 163 banded, mimicking sedimentary features of the precursor limestone but frequently show post-164 depositional brecciation and recrystallization. Mineralization becomes progressively surrounded 165

by recrystallized limestone to coarse grained marble and garnet skarn approaching the PegasoZone.

#### 168 *Local stratigraphy*

Mineralization at Cinco de Mayo is related to the interplay between ore-fluids related to 169 Cenozoic silicic magmatism and Jurassic-Cretaceous limestones, clastic sediments and 170 evaporates deposited in the Jurassic Chihuahua Trough deformed by Laramide compression. The 171 evaporite sequences are dominated by gypsum and/or anhydrite with interbedded shale, whereas 172 173 the clastic sediments are composed of conglomerate sandstone, siltstone and shale (Selway and 174 Leonard, 2008). Cinco de Mayo mineralization is hosted by thrusted Cretaceous fossiliferous limestone units of Early to Middle Albian age (Table 1). Although the deformation renders 175 precise correlation with the regional stratigraphy somewhat challenging, exposed limestones are 176 177 interpreted to include the Late Aptian Cuchillo Formation at the base, overlain by the Benigno, Lagrima, and Finlay Formations. The Late Albian Benavides Shale caps the sequence. The 178 Finlay Formation is the most important host for mineralization. It is a relatively clean limestone 179 with local cherty beds, high energy beach zones and reefs (Lyons, 2008). The overlying 180 Benavides Shale consists mostly of shale and may have played an important role as an aquitard 181 capping hydrothermal fluid movements during mineralization. The upper Albian and 182 Cenomanian Loma de Plata, Ojinaga and Indidura Formations of the regional stratigraphy are not 183 reported in outcrop at Cinco de Mayo (Lyons, 2008). 184

#### METHODS

186 *Samples* 

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187 Wall rock carbonate and vein calcite samples were taken from half-core from 16 drill holes located through the NW-SE trending Pegaso Zone and along a ~12 km NNW-SSE trending 188 transect from the Pegaso Zone to the most distal drill hole in the far SE corner of the Cinco de 189 Mayo property. Six additional drill holes from the vicinity of the two transects were also sampled 190 (Fig. 1). Based on the location relative to the Upper Manto/Pegaso Zone mineralization, these 191 drill holes are labelled 'mineralization zone', 'proximal', and 'distal', respectively. 192 Mineralization zone samples are dominantly from the Pegaso Zone (CM07-20, CM12-423, 193 CM12-431, CM12-428, and CM11-380) together with additional samples from the Pozo Seco 194 Zone (CM10-247). Proximal samples are dominantly from drill holes located to the S and SE of 195 196 the Pegaso Zone (CM06–01, CM10–317, CM10–305, CM10–127, and CM10–292) and define a transect bridging the area between the mineralization and the distal drill holes (CM09-88, 197 CM09–89, and CM09–94) in the SE corner of the property. This transect is parallel to the general 198 strike of thrusting in the area and was chosen to discern the extent of fluid flow and stable 199 200 isotope alteration in the subsurface. CM08-45 is located to the NW of the Pegaso Zone and was regarded as the 'most barren looking hole' on the Cinco de Mayo property during exploration 201 drilling (Megaw, pers. comm.) and was initially expected to reflect the local stable isotope 202

background. However, its stable isotope values fall in the "proximal" range. Thus, CM09–94,
which shows the least isotopically altered values, was taken as the stable isotope background
against which the composition of all other samples are compared.

Stable isotope analyses were conducted on carbonate powder drilled from selected sites on solid half–core samples using a handheld Dremel<sup>™</sup> tool. The drill bit was cleaned in 10% HCl and ethanol after each sample to avoid cross–contamination between samples. Sites for micro– sampling were chosen based on macroscopic investigation of half–core samples under normal and UV light and assay data provided by MAG Silver. Micro sampling sites include different vein generations and their respective wall rocks.

212 *Macroscopic investigation* 

For initial investigation half-core samples were chosen based on downhole location to allow for even spacing, with increased density near mineralization. Subsequent sampling focused on vein-wall rock pairs from the Finlay Formation. Samples were photographed under normal and UV light to identify micro sampling sites and distinct vein generations based on UV fluorescence color and intensity, cross-cutting relationships, deformation features, and the macroscopic appearance of the vein-wall rock interface.

#### 219 *Stable isotope analysis*

220 Approximately 35 mg of carbonate powder was placed into unflushed 12 mL Labco borosilicate glass vials that were sealed with butyl rubber septa. About 15 drops of 85% H<sub>3</sub>PO<sub>4</sub> 221 was injected into each vial through the rubber septum and left to react with the carbonate powder 222 for ~1 hour on an aluminium block heated to 72°C. Following digestion, sample gas released 223 224 from the dissolved carbonate was introduced into an off-axis integrated cavity output spectrometer (OA-ICOS; Los Gatos Research (LGR) model 908-0021 and CCIA-46) via a 225 stainless steel tubing line with a cold trap to freeze out water vapor (Barker et al., 2011). The 226 OA-ICOS instrument simultaneously measures the volume fraction of CO<sub>2</sub> isotopologues 227 (<sup>12</sup>C<sup>16</sup>O<sup>16</sup>O, <sup>13</sup>C<sup>16</sup>O<sup>16</sup>O, <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O) by high-resolution laser absorption in the near-infrared 228 range. A more detailed summary of the OA-ICOS theory and its application to carbonate 229 minerals can be found in Baer et al. (2002) and Barker et al. (2011). LGR model 908-0021 is 230 incapable of accurately measuring the isotope composition of CO<sub>2</sub>-H<sub>2</sub>S mixtures, which results 231 from acid digestion of sulfide-bearing carbonate samples. These samples were analyzed using a 232 second generation ICOS instrument (LGR CCIA-46), equipped with a modified laser system that 233 avoids laser absorption by H<sub>2</sub>S (Beinlich et al., 2017). The stable isotope composition is reported 234 as  $\delta$ -values in per mil (‰), i.e. as parts per thousand difference from a standard (Faure and 235 Mensing, 2005): 236

237 
$$\delta X = [(R_{sample}/R_{standard})-1] \times 10^3,$$

where X denotes <sup>13</sup>C or <sup>18</sup>O and R is <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O, respectively. Throughout the text we 238 describe relatively high  $\delta$ -values as 'heavy' or 'enriched' and relatively low  $\delta$ -values as 'light' 239 or 'depleted'. Repeated analyses of the UBC-MDRU calcite in-house standard BN13 indicate 240 that the measurements are accurate with a standard error of 0.6% (1 SE) for  $\delta^{18}$ O and 0.5% (1 241 242 SE) for  $\delta^{13}$ C (Barker et al., 2011). All isotope values in this report are standardized to Vienna Standard Mean Ocean Water (VSMOW) and Vienna Pee Dee Belemnite (VPDB) for oxygen and 243 carbon, respectively. The standard deviation given in the text refers to the 68% confidence 244 interval (1 $\sigma$ ). A total of 910 O and C isotope analyses were conducted for this study. 245

#### 246 *Trace–element analysis*

247 Laser ablation ICP-MS measurements of a series of trace-elements was carried out using a ASI Resolution S155–SE laser ablation system, based on a 193 nm ArF excimer laser (ATL) 248 attached to a N<sub>2</sub> purged-beam delivery unit at the University of Waikato, New Zealand. A spot 249 size of 100 µm and laser fluence of ~6 J cm<sup>-2</sup> was used. Ablation took place in a two-volume 250 cell, developed by Laurin Technic (Müller et al., 2009). Before analysis, the cell was vacuum 251 purged and then filled with He, which washed the ablated aerosol out of the cell. The carrier gas 252 253 was mixed with Ar in the cone that sits above the zone where ablation takes place, and was then mixed downstream with a small amount of N2 (6 mL per minute) to increase plasma temperature 254 255 (Hu et al., 2008). The ablation aerosol was transported through a nylon manifold signal smoothing device ("squid") before reaching the torch of a Perking Elmer Elan II ICP-MS. The 256 257 ICP-MS was tuned using NIST 612 glass for high sensitivity and low oxide production rates (ThO/Th <0.5%). The quadrupole mass analyzer sequentially peak shifts between masses of 258 interest (Mg, Si, P, S, Mn, Fe, Cu, Zn, As, Sr, Y, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, 259 Tm, Yb, Hf, Tl, Pb, Th, U) during the laser ablation process, with a sweep time over the entire 260 mass range of less than 1 second. 40 seconds of laser ablation data was collected for each 261 262 analysis point, and at least 20 seconds of gas blank were collected for each sample. The ICP-MS 263 collected data continuously in time-resolved analysis mode, with gas blanks collected before and after each laser ablation point to facilitate blank subtraction. NIST 612 was used as a calibration 264 standard. Data reduction followed established protocols for time-resolved analysis (Longerich et 265 al., 1996). Iolite software (Hellstrom et al., 2008) was used for data reduction, with <sup>43</sup>Ca used as 266 an internal standard. Carbonate minerals were assumed to be pure calcite, with Ca = 40.04 wt % 267 for the internal standard. As laser ablation ICP-MS results are reported relative to the external 268 standard value, a  $\pm 5\%$  variation in this value will lead to an uncertainty of ~ 13% in the 269 calculated trace-element concentrations. 270

#### 271

#### RESULTS

Stable isotope analysis was initially focused on identifying the preferential fluid flow path at Cinco de Mayo by sampling at high spatial resolution at intervals between 2 m and 7 m and across formation boundaries. Based on the variability and absolute values of stable isotope ratios,

we identified the Finlay Formation as the principal aquifer, which then became the main focus of 275 subsequent sampling. The downhole distribution of O and C isotope ratios in vein and wall rock 276 samples of the most mineralized drill hole (CM12-431) was compared with that of the least 277 altered drill hole (CM09–94) in Figure 2, showing the distribution of stable isotope ratios across 278 279 several limestone formations. The stable isotope ratios of the non-aquifer formations (Table 2) are generally higher and show less dispersion with depth than those of the Finlav Formation. The 280 spreads in O and C isotope ratios of all Finlay wall rock and vein samples are shown as box plots 281 in Figure 3 in the general order of increasing distance from CM12-431. CM12-431 has been 282 chosen as the point of "origin" due to the presence of strong mineralization surrounded by 283 hundreds of metres of pervasive marble, hornfels and skarn alteration indicating proximity to the 284 likely heat and fluid source. CM10-247 is situated in a different mineralization zone 4 km to the 285 W (Pozo Seco Zone) but is considerably altered and is therefore placed to the left of CM12-431 286 in Figure 3. 287

#### 288 Local stable isotope background – distal hole CM09–94

The local stable isotope background is defined as the composition of distal hole CM09–94 in the SE part of the Cinco the Mayo property. The distance of CM09–94 to the Pegaso Zone is ~12.7 km. CM09–94 intersects the Benavides, Finlay and Lagrima Formations, all of which have constant  $\delta^{13}$ C and  $\delta^{18}$ O values throughout the entire length of the core (Fig. 2A). Averaged wall rock  $\delta^{13}$ C and  $\delta^{18}$ O values are 3.1±0.7‰ and 22.4±1.7‰, respectively (n = 72). The composition of the Finlay limestone in CM09–94 is shown in Figure 3A (Table 3).

#### 295 Proximal and distal drill holes

The distal and proximal drill holes show average  $\delta^{13}$ C and  $\delta^{18}$ O values slightly below the 296 local stable isotope background defined by CM09–94. The variations of isotope ratios with depth 297 in these holes are more pronounced than in CM09-94. CM10-305 and CM10-292 are mostly 298 within the Finlay Formation, CM09-127 intersects the Benavides, Finlay, Lagrima, and Benigno 299 Formations and CM09-88 cut just the Benigno and Cuchillo Formations. CM08-45 and CM10-300 332 are located ~3 km to the NW and W from the Pegaso Zone, respectively. Samples from these 301 302 two drill holes are from the Finlay Formation and are significantly depleted in <sup>18</sup>O and slightly 303 depleted in <sup>13</sup>C relative to the local background. CM06–01 is located directly to the SW of the Pegaso Zone. The average Finlay wall rock  $\delta^{13}$ C values for proximal samples vary between 304  $0.9\pm1.2\%$  and  $2.7\pm0.8\%$ ,  $\delta^{18}$ O values vary between  $15.5\pm2.9\%$  and  $20.8\pm1.3\%$  (Fig. 3A; Table 305 3). 306

307 *Mineralization zone samples* 

Most of the investigated mineralization zone samples intersect the Pegaso Zone with one additional sample from the Pozo Seco Zone. Mineralization zone samples are characterized by highly variable isotope ratios with variations of up to 10% for both oxygen and carbon over depth intervals of 10 m or less (Fig. 2B). Average stable isotope ratios (shown as the five point moving average in Fig. 2) are significantly shifted to lower values compared to the local stable isotope background and proximal samples. CM12–431 intersects three mineralized zones where carbonate has been completely replaced by massive sulfide on the meter to tens of meters scale. The contact between massive sulfide and limestone host rock in CM12–431 is often characterized by meter wide zones of white recrystallized calcite. Samples from these contact zones display the most depleted values, to as low as  $\delta^{13}C = -6\%$  and  $\delta^{18}O = 10\%$ .

The depth interval with the strongest variation and lowest average stable isotope ratios 318 coincides with intervals having high metal (e.g. Ag in Fig. 2B) and S concentrations within 319 CM12-431 and CM12-423. Even though stable isotope alteration is preferentially developed in 320 the Finlay Formation, it extends into the underlying Lagrima shale and Benigno limestone (Fig. 321 2B). Samples from the stratigraphically higher Benavides shale are often characterized by low 322 323 carbonate mineral abundance and only a small number of samples could be analyzed owing to the lack of carbonate minerals. Average stable isotope ratios of Finlay limestone in CM12-431 324 and CM12–423 are  $\delta^{13}C = 1.8 \pm 1.2\%$  (n = 43),  $1.9 \pm 1.2\%$  (n = 90) and  $\delta^{18}O = 17.2 \pm 2.7\%$  and 325 19.6±2.2‰, respectively (Fig. 3A; Table 3). The isotope ratios gradually increase with depth and 326 327 approach values identical to the local stable isotope background. This transition zone has a thickness of ~200 m in both drill holes (Fig. 2B; only shown for CM12-431). CM10-247 from 328 the Pozo Seco Zone intersects the Finlay, Lagrima, Benigno, and Cuchillo Formations. The 329 isotope ratios are consistently offset to lower values throughout the entire core and do not 330 increase at depth (Tables 2 and 3). The average Finlay wall rock  $\delta^{13}$ C is 2.5±0.7‰ and  $\delta^{18}$ O is 331 14.5±1.3‰ (Figs. 2 and 3). 332

#### 333 *Vein generations*

Three generations of carbonate veins could be distinguished at Cinco de Mayo based on macroscopic textural observations and UV fluorescence. Throughout the following text, the different vein generations are referred to as G1, G2 and G3 veins with G1 being the first (oldest) and G3 the last (youngest) generation.

*Generation 1 veins.* The first vein generation displays a white color under normal light and shows evidence of ductile deformation, i.e. is often boudinaged and/or folded on hand specimen scale. Interfaces between G1 veins and their wall rocks are typically diffuse. G1 veins are cross– cut by later, texturally distinct, vein generations G2 and G3 (Fig. 4A–C). Based on hand specimen observations, G1 veins are pure calcite and sulfide minerals have not been found in this vein type. The majority of veins showing these textural features are generally UV inactive but a very weak pink fluorescence was locally observed (Fig. 4A).

345 *Generation 2 veins.* On hand specimen scale, G2 veins are either straight or show evidence 346 of brittle deformation. Interfaces with the surrounding wall rock are always sharp. G2 veins 347 usually show a strong pink, or sometimes a blue UV fluorescence color and are rarely UV inactive (Fig. 4B–F). Where cross–cutting relationships are evident, G2 veins are consistently younger than G1 veins. Heavily veined samples sometimes exhibit mutual cross–cutting relationships of veins consistent with the textural characteristics of G2 veins (Fig. 4F). These cross–cutting G2 veins have been arbitrarily classified as vein types G2a and G2b with G2b veins being younger. G2 veins frequently contain uncharacterized sulfide minerals and ankerite in addition to calcite.

*Generation 3 veins.* This third vein generation is distinguished based on textural relationships with sulfide minerals. While G2 veins are frequently sulfide bearing, G3 veins cross-cut sulfide minerals and zones of massive sulfide mineralization. Such G3 veins are undeformed and sometimes show a weak pink UV fluorescence color (Fig. 4G and F). Interfaces with the surrounding sulfide host mineral are sharp and ankerite has not been detected in G3 veins. However, the absence of cross-cutting relationships means textural classification criteria alone are insufficient to distinguish G2 and G3 veins outside of mineralized zones.

#### 361 *Vein carbonate stable isotope ratios*

The stable isotope ratios of all analyzed calcite veins and their classification into the three 362 vein generations is shown in Figure 5. The downhole distribution of vein calcite stable isotope 363 ratios is shown for cores CM12-431 and CM09-94 in Figure 2. G1 veins show a wide spread of 364 positively correlated  $\delta^{13}$ C and  $\delta^{18}$ O values ranging from -4‰ to 3‰ and 15‰ to 22‰, 365 respectively (Fig. 5). G2 veins show a similar spread in  $\delta^{13}$ C values between -3‰ and 4‰, while 366  $\delta^{18}$ O values vary between 10% and 18%. The compositional ranges of the two vein generations 367 overlap but cluster in distinct areas on a  $\delta^{18}$ O vs.  $\delta^{13}$ C plot (Fig. 5). The stable isotope 368 composition of G2b veins overlaps with that of G2a veins and ranges in  $\delta^{13}$ C between 1.5‰ and 369 2.5‰ and in  $\delta^{18}$ O between 14‰ and 19‰ (Fig. 5). G3 veins have a distinct stable isotope 370 composition that is strongly depleted in both <sup>13</sup>C and <sup>18</sup>O relative to G1 and G2 veins.  $\delta^{13}$ C 371 values vary between -3‰ and -1‰,  $\delta^{18}$ O between 8‰ and 13‰ (Fig. 5). The isotopically distinct 372 composition of G3 and G2b veins supports their classification as separate generations. The 373 compositional overlap of G3 veins with depleted G2a veins complicates their classification and a 374 375 definitive classification is not always possible. Isotope ratios of G2 veins hosted in Finlay limestone are shown as box plots in Figure 3B. 376

#### 377 Vein carbonate trace–element concentrations

Vein carbonate trace–element concentrations were measured on representative samples of the three vein generations and from mineralization zone, proximal and distal cores. Concentrations were measured for Mg, Si, P, S, Mn, Fe, Cu, Zn, As, Sr, Y, Ba, Hf, Tl, Pb, Th, U and rare earth elements (REE). Generally, trace–element concentrations are low except those of Si, Mg, Fe and Mn (435 – 4050 ppm). Sulfur and Sr concentrations range between 30 ppm and 10 ppm, concentrations of all other analyzed elements are below 10 ppm and mostly also below 1 ppm. In most samples P, Hf, Tl, and Th are below detection limits. Likewise, the heavy REE (HREE) Tm and Yb are generally near or below their detection limits (~ 0.03 ppb). Average
 trace-element concentrations on a per-vein basis are summarized in Table 4.

Systematic trace-element concentration differences exist between the different vein 387 generations. The average concentrations of all analyzed trace-elements are enriched in G2 and 388 G3 veins relative to G1 veins except Sr, which has similar concentrations in all three vein 389 generations. The strongest enrichment (> 10 times enriched) in average concentrations in G2 390 relative to G1 veins is found for Mn, Fe, Y and REE. Mg, Cu, Zn, Pr, Sm, Ho and Er are 391 392 moderately enriched (5-10 times), while the remaining trace-elements show a slight (<5 times) enrichment. Trace-element concentrations in G3 veins are on average lower than in G2 veins. 393 However, G3 vein concentrations of S, As, Sr, La, Ce, Eu and Pb are weakly (< 2.7 times) 394 enriched or similar compared to G2 veins (Table 4). In addition, there is an observable 395 enrichment trend in veins from distal through proximal to mineralization zone samples. The 396 highest vein calcite trace-element concentrations are found in G2 veins in CM12-431. 397

REE concentrations normalized to Post-Archaean Australian Shale (PAAS; McLennan, 398 1989) show relatively similar values for light REE (LREE) and HREE, while in some veins Eu 399 400 and sometimes also the neighbouring REE show a relative enrichment (Fig. 6). This enrichment is not systematic with respect to vein generation and distance to the mineralization zone. In 401 402 contrast, absolute REE concentrations show systematic variations with respect to the vein paragenesis and distance from the mineralization zone. G2 veins from the mineralization zone 403 404 show the highest REE concentrations and G2 veins are always enriched relative to G1 veins. However, REE concentrations in G2 veins from the Pozo Seco Zone mineralization (CM10-247) 405 are similar to G1 veins from the Pegaso Zone mineralization and proximal and distal G2 veins, 406 but are lower than most Pegaso Zone G2 veins (Figure 7). 407

408

#### DISCUSSION

409 *Correlation between the local, regional and global stable isotope background* 

410 The least altered drill hole at Cinco de Mayo (CM09–94) shows average isotope ratios for Finlav limestone of  $\delta^{13}C = 2.9 \pm 0.6\%$  and  $\delta^{18}O = 22.4 \pm 1.3\%$ . In comparison, global scale C and 411 O isotope ratios of Cretaceous limestone range between -5‰ and 5‰ for  $\delta^{13}$ C and 23‰ and 412 30‰ for  $\delta^{18}$ O (Veizer et al., 1999). While  $\delta^{13}$ C values of the least altered Finlav limestone are 413 consistent with the global average ( $\delta^{13}C = 2.4\%$ ),  $\delta^{18}O$  is considerably depleted (global average 414  $\delta^{18}O = 27.7\%$ ). This shift in  $\delta^{18}O$  values suggests isotope exchange on a scale larger than the 415 alteration associated with mineralization at Cinco de Mayo, i.e. on a regional scale. The presence 416 of G1 veins that show evidence for ductile deformation (folded, boudinaged) and an isotope 417 composition similar to the local least altered limestone suggests that the shift to lower  $\delta^{18}$ O took 418 419 place during carbonate diagenesis.

Megaw (1990) reported stable isotope ratios for barren Finlay limestone from the Santa 420 Eulalia mining district, ~250 km to the S of Cinco de Mayo, that are -0.8‰ for  $\delta^{13}$ C and 21.8‰ 421 for  $\delta^{18}$ O. (Sweeney, 1987) reported  $\delta^{13}$ C values of 1‰ and  $\delta^{18}$ O values of 18‰ for unaltered 422 Finlay limestone from the Naica district, ~350 km to the S of Cinco de Mayo. While there is 423 424 general agreement between the three sites, stable isotope ratios of least altered limestone from Cinco de Mayo are slightly higher than those from Santa Eulalia and Naica. The reason for these 425 slight differences may simply reflect heterogeneous alteration during carbonate diagenesis or 426 weak alteration of distal rocks during mineralization at Santa Eulalia and Naica. The least altered 427 428 Finlay samples used by Megaw (1990) to define the Santa Eulalia C and O isotope background were sampled at a distance of ~5000 m from the mineralization zone. It can be speculated that 429 this sample was exposed to distal stable isotope alteration despite the absence of visible 430 mineralization given the size of previously documented <sup>18</sup>O alteration halos in carbonate rocks 431 (Barker et al., 2013; Kesler et al., 1995). Further sampling of regional rocks thought to be 432 433 unaffected by hydrothermal alteration would be needed to confidently establish a regional vs. local background. Here, we assume that the local  $\delta^{18}$ O background is ~ 22‰. 434

#### 435 Constraints on the stable isotope composition and temperature of the mineralization fluid

The decrease of vein and wall rock stable isotope ratios in the proximity to mineralization 436 is consistent with isotope exchange reactions driven by an isotopically light fluid. The stable 437 isotope composition of G2 vein calcite (frequently with sulfide minerals) from the mineralization 438 439 zone can be taken as synchronous with sulfide precipitation and used to constrain the 440 composition and source of the incoming mineralization fluid. G1 veins are likely related to diagenesis and G3 veins postdate mineralization and may represent late stage fluid flow or be 441 completely unrelated. The composition of G2 veins from the mineralization zone clusters around 442 -1‰ for  $\delta^{13}$ C and 13‰ for  $\delta^{18}$ O (Figs. 2, 3 and 5) and this composition in combination with 443 fluid-calcite O isotope fractionation factors can be used to constrain the stable isotope 444 445 composition of the vein forming and mineralizing fluid. However, the derived constraints are based on the assumption that isotopic equilibrium was attained during the alteration and are thus 446 subject to uncertainty. 447

448 The mineralization temperature at Cinco de Mayo is unconstrained but a range of 250°C to 500°C is accepted for most carbonate hosted Ag-Pb-Zn-Cu deposits in northern Mexico 449 (Haynes and Kesler, 1988; Megaw et al., 1988). Adopting this temperature range and suitable 450 calcite-fluid O isotope fractionation factors (Chacko et al., 2001) in combination with the 451 452 measured O isotope ratio of vein calcite (~13‰) indicate an O isotope ratio of the alteration fluid between 5.7‰ (250°C) and 11.2‰ (500°C). If it is assumed that the infiltrating fluid was 453 magmatic ( $\delta^{18}O = 7\%$  - 9%; Taylor, 1974), then the observed vein calcite  $\delta^{18}O$  values would be 454 in equilibrium with magmatic fluid at temperatures between ~290°C and ~360°C. Within the 455 456 discussed uncertainties, the oxygen isotope composition of G2 vein calcite is therefore consistent with a dominantly magmatic source for the mineralizing fluid. A similar conclusion was reached
for limestone alteration at Providencia, northern Mexico (Rye, 1966; Rye and O'Neil, 1968).

#### 459 Fluid flow model for isotope alteration

Hydrothermal limestone alteration proceeds as dissolution-precipitation reaction allowing 460 for isotope exchange between the solid and fluid. The intensity of stable isotope alteration and 461 the propagation distance of the alteration front from the fluid inlet depend on the fluid volume, 462 the relative difference in solid and fluid compositions, temperature, rates of fluid-mineral isotope 463 464 exchange, and the transport mechanism. A conceptual, 1-dimensional reactive transport model for infiltration of an isotopically light, magmatic fluid into isotopically heavy limestone is shown 465 in Figure 9. This model is only an approximation because the 1-dimensional flow vector cannot 466 capture complex natural fluid dynamics resulting from heterogeneities in the aquifer 467 permeability. Keeping these uncertainties in mind, the model provides a framework that allows 468 relating the measured stable isotope composition of altered wall rock and vein samples to the 469 progressively changing isotopic composition of the reactive alteration fluid. Rates of fluid-470 mineral isotope exchange are related to transport rates using the dimensionless Damköhler 471 number (N<sub>D</sub> = reaction rate/transport rate). A high N<sub>D</sub> (N<sub>D</sub>  $\geq$  ~10) indicates instantaneous 472 reaction and transport limited reaction front propagation, whereas the isotope alteration front lags 473 behind the fluid front at low  $N_D$  ( $N_D < 1$ ). The dimensionless Peclet number describes the relative 474 proportion of advective to diffusive isotope transport ( $N_{Pe}$  = advective transport rate/diffusive 475 476 transport rate) and controls the sharpness of isotope ratio gradient along the flow path. The length scale of front propagation is a function of the total fluid volume involved in the alteration, 477 expressed as time-integrated fluid flux (TIFF in cm<sup>3</sup>/cm<sup>2</sup>) reflecting the total fluid volume (cm<sup>3</sup>) 478 479 entering the aquifer per unit area (cm<sup>2</sup>) at the fluid inlet. Details on the modelling approach can be found elsewhere (e.g., Bowman et al., 1994; Dipple and Ferry, 1992a; Knoop et al., 2002; 480 481 Lassey and Blattner, 1988).

Near the fluid source, a large flux of externally buffered fluid that is compositionally 482 distinct from the infiltrated limestone promotes pervasive wall rock alteration. If isotopic 483 equilibrium is attained during wall rock alteration and vein calcite precipitation, both will have 484 identical isotope ratios ( $\Delta^{18}O_{WR-vein} \approx 0$ ) at low wall rock  $\delta^{18}O$  (Fig. 9A and B). The isotope ratio 485 of the alteration fluid will increase with distance to the fluid inlet as a result of isotope exchange 486 reactions with the limestone wall rock and of mixing with pre-existing pore-fluid that is in 487 equilibrium with the unaltered limestone and hence isotopically heavier than the incoming 488 magmatic fluid. Thus, even pervasively altered distal rocks will be characterized by isotope ratios 489 in between those near the fluid inlet and unaltered distal rocks. Progressive fluid-rock interaction 490 along the flow path will shift the fluid isotope composition closer to its equilibrium value with 491 the wall rocks and diminish its alteration capacity. Sluggish reaction kinetics will then produce 492 vein calcite that is isotopically light relative to its moderately altered wall rock ( $\Delta^{18}O_{WR-vein} > 0$ ) 493 (Fig. 9A and B). When the alteration fluid composition approaches equilibrium with the 494

limestone, vein calcite will be isotopically identical to its unaltered wall rock ( $\Delta^{18}O_{WR-vein} = 0$ ) at high wall rock  $\delta^{18}O$  (Fig. 9A and B). The position of this point in space defines the limit of the stable isotope alteration footprint. Scenarios for different values of N<sub>Pe</sub> and N<sub>D</sub> are shown in Figure 9.

 $\Delta^{18}O_{WR-vein}$  values of distal, proximal and mineralization zone samples display a positive 499 correlation with  $\delta^{18}O_{WR}$  (Fig. 10A), which is consistent with the conceptual model (Fig. 9). 500 Mineralization zone samples are characterized by low  $\Delta^{18}O_{WR-vein}$  at low  $\delta^{18}O_{WR}$ , indicating 501 proximity to the fluid inlet, whereas distal samples show low to intermediate  $\Delta^{18}O_{WR-vein}$  values 502 at high  $\delta^{18}O_{WR}$ . However, a number of samples display negative  $\Delta^{18}O_{WR-vein}$  values and therefore 503 appear inconsistent with the theory (Fig. 10A). Negative  $\Delta^{18}O_{WR-vein}$  values may result from 504 erroneous vein generation classification, or represent a different snapshot of the same alteration 505 event. Pulsed fluid supply and/or fracture healing and vein calcite formation at different times 506 can form isotopically distinct veins representing the dynamically changing fluid composition 507 during the alteration (see Bowman et al., 1994 for discussion). Continued wall rock alteration 508 may then result in the observed negative  $\Delta^{18}O_{WR-vein}$  values. The majority of seemingly 509 inconsistent vein-wall rock pairs are from CM10-247 (Pozo Seco Zone) and comprise strongly 510 511 altered wall rock and less depleted veins that are compositionally and texturally distinct from G1 veins. These samples are therefore indicative of early vein formation predating the final isotope 512 alteration of the surrounding wall rock. This rationale also applies to samples from CM12-423 513 and CM12–431. Negative  $\Delta^{18}O_{WR-vein}$  values from CM09–89 represent isotopically heavy veins 514 in slightly altered limestone wall rock. As for negative  $\Delta^{18}O_{WR-vein}$  values from the mineralization 515 zone, isotopically heavy veins in CM09-89 may represent an early stage of vein formation. 516 Alternatively, the veins may be diagenetic G1 veins that show textural characteristics of G2 veins 517 (Fig. 10A). 518

Vein-wall rock pairs that appear to record the final alteration progress (i.e. positive 519 520  $\Delta^{18}O_{WR-vein}$ ) allow for the evaluation of fluid volume and reaction kinetics and can thus aid in interpreting individual samples within the context of the larger scale hydrothermal system. Figure 521 10B shows vein–wall rock pairs with  $\Delta^{18}O_{WR-vein} > 0$  together with contours outlining Damköhler 522 numbers and the TIFF-normalized distance (distance/TIFF) from the fluid inlet. The volume of 523 fluid (TIFF) driving the isotope alteration front is approximately proportional to its propagation 524 distance from the source (Hofmann, 1972). Hence, pervasively altered mineralization zone 525 samples plot at low z/TIFF values, whereas moderately altered proximal and distal samples plot 526 at higher z/TIFF values. Figure 10B can be used to approximate the TIFF if the distance of the 527 sample to the assumed fluid inlet is known. For example,  $\Delta^{18}O_{WR-vein}$  and  $\delta^{18}O_{WR}$  values of 528 CM09–89 (z =  $\sim 10.6$  km) plot between 0.3 and 0.5 (Fig. 10B) suggesting a TIFF of  $2.1 \times 10^6$ 529 cm<sup>3</sup>/cm<sup>2</sup> to 3.5×10<sup>6</sup> cm<sup>3</sup>/cm<sup>2</sup>. Flux estimates based on the composition and location of CM10-530 292 and CM08–45 yield similar results. This estimate is consistent with crustal fluid flux during 531 regional metasomatism and contact metamorphism (Ague, 1997; Dipple and Ferry, 1992b; Ferry 532 and Dipple, 1991), including carbonate hosted systems (Ferry et al., 2002). Furthermore, the 533

position of  $\Delta^{18}O_{WR-vein}$  vs.  $\delta^{18}O_{WR}$  pairs in Figure 10B reflects the rate of isotope exchange reactions between the fluid and wall rock along flow through the aquifer. Fast reactions result in  $\Delta^{18}O_{WR-vein}$  vs.  $\delta^{18}O_{WR}$  pairs plotting at high N<sub>D</sub>, while sluggish reactions plot at low N<sub>D</sub> (Fig. 10B). Figure 10B therefore indicates changing reaction kinetics from fast within the mineralization zone to sluggish in distal parts of the system, potentially related to fluid cooling along its flow path.

In summary, the measured oxygen isotope composition of Cinco de Mayo wall rock and 540 541 vein calcite samples is consistent with a simple 1-dimensional fluid flow and alteration model (Fig. 11A and B). CM09-94 represents the least altered background based on only a small 542 isotope ratio dispersion with depth, similar vein and wall rock compositions and the high wall 543 rock O isotope ratios. In most cases, proximal and mineralization zone samples show isotopically 544 depleted veins and relatively strong variations of depleted wall rock O isotope values. The 545 compositional variations between veins and wall rocks indicates that close to equilibrium 546 conditions have been reached locally (Fig. 10B); consistent with the presence of preferential fluid 547 pathways. CM09-89 represents the most distal part of the system where stable isotope alteration 548 is detectable and thus defines the extent of the stable isotope alteration footprint at ~11 km from 549 550 the mineralization zone (Fig. 11A and B). The large size of this <sup>18</sup>O depletion halo may be explained by the presence of a large fluid flow system requiring pore space connectivity on the 551 km scale or fluid infiltration into the Finlay Formation at multiple, potentially structurally 552 controlled, fluid inlets. However, the outlined consistency of the distribution of isotopic 553 554 alteration with a simple 1-dimensional flow system and the concentrated occurrence of hornfels alteration and mineralization indicative of a localized heat and fluid source imply that large scale 555 limestone stable isotope alteration at Cinco de Mayo was facilitated by overall fluid connectivity. 556

#### 557 *Correlation of vein calcite trace–element concentrations with stable isotope ratios*

The inverse correlation of vein calcite trace-element concentrations with respective O 558 isotope ratios corroborates the link between mineral deposit formation and limestone stable 559 isotope alteration. This correlation is most strongly developed for Zn, Mn, As, Fe, Y and Pb 560 561 concentrations. Despite considerable spread even on the per-vein basis, trace-element 562 concentrations in mineralization zone G2 veins from cores CM12-431 (and sometimes also CM12–423) are typically two orders of magnitude higher than in G1 veins and distal G2 veins. 563 However, mineralization zone hole CM11-380 shows both low  $\delta^{18}O_{\text{vein}}$  and trace-element 564 concentrations (Fig. 8; Table 4). Trace-element enrichment in G2 veins, particularly within the 565 mineralization zone is consistent with their strong fluorescence under UV light. Manganese 566 substitution is a common cause of fluorescence in carbonates together with other activators 567 including REEs, Zn and lattice defects (Gies, 1975; Schulman et al., 1947). The high Fe 568 concentration in G2 veins is consistent with the presence of abundant ankerite (Table 4). 569

REE concentrations and their ratios including Ce<sub>N</sub>/Ce<sub>N</sub><sup>\*</sup> and Eu<sub>N</sub>/Eu<sub>N</sub><sup>\*</sup> appear to vary non-570 systematically with position along the hydrothermal flow path, vein generation and  $\delta^{18}O_{vein}$  (Fig. 571 8). However, the G3 vein in CM12-431 shows significantly elevated La/Nd, La/Yb, Eu<sub>N</sub>/Eu<sub>N</sub>\* 572 and low  $Ce_N/Ce_N^*$  compared to all other analyzed veins. This vein has also the lowest  $\delta^{18}O$  value, 573 574 which corroborates the distinction of G3 veins as individual group. Figure 6 shows that a positive Eu-anomaly has preferentially developed in G2 veins relative to G1 veins from the same hole. 575 For example, G1 veins from CM12-431, CM12-423 and CM06-01 show no or only a weak Eu-576 anomaly, whereas G2 veins from these holes show a distinct Eu-anomaly with the exception of 577 one G2 vein in CM12–423 (Fig. 6). Generally, the relatively flat REE pattern of vein calcite may 578 result from the presence of excess Ca<sup>2+</sup> relative to CO<sub>3</sub><sup>2-</sup> in the alteration fluid. Calcite 579 preferentially incorporates Eu<sup>3+</sup> and the Eu–anomaly present in only some of the G2 veins may 580 indicate their formation prior to G2 veins lacking the Eu-anomaly, which may be related to 581 cooling-induced reduction of Eu<sup>3+</sup> and/or decreased ligand concentrations (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>) 582 583 (Bau, 1991). The relatively low  $Ce_N/Ce_N^*$  (~ 0.75) in G3 vein calcite from CM12–431 suggests reducing conditions of late stage fluid, which may be unrelated to mineralization but is consistent 584 with cooling of the system during or after mineralization (Bau and Möller, 1992). 585

#### 586 Implications and application of carbon and oxygen isotopes to mineral exploration

587 The results of this study show that stable isotope analysis of vein and wall rock carbonate provides insight into the nature and extent of hydrothermal systems. Detailed analysis of vein 588 589 samples and vein-wall rock pairs appear to have promise for mineral deposit vectoring. The offset between the global isotopic reference frame and the inferred least altered samples at Cinco 590 de Mayo and other deposits (cf. Santa Eulalia, Naica, Providencia) underscores the need during 591 mineral exploration stable isotope programs for defining the local background against which 592 mineralization-related changes in stable isotope ratios can be compared. Relative to global 593 594 values, the least altered samples may appear strongly altered but that shift in stable isotope ratios is likely unrelated to mineralization and therefore may be misleading. This can be achieved by 595 taking several tens of samples per limestone unit at progressive distances sufficiently far away 596 from the assumed center of mineralization (>10 km) to avoid distal intrusion-related alteration. 597 598 Once the extent of the isotope alteration halo is established, preferential fluid flow paths can be delineated by systematic high resolution sampling at  $\sim 5-10$  m depth intervals of 1 to 3 complete 599 drill holes from within the alteration halo. Additional sampling may then target vein-wall pairs 600 from the aquifer every 2 - 3 km at coarser spacing of  $\sim 10$  pairs per drill hole, depending on 601 aquifer thickness. These will reveal isotopic gradients that vector towards mineralization and 602 reflect the alteration intensity and fluid volumes involved (Fig. 10). Large ore deposits are 603 604 unlikely to form from small fluid volumes, so constraining the volume of alteration fluids is important because large-scale pervasive isotope alteration requires a large fluid flux, which in 605 turn increases the likelihood for larger volumes of contained metal (Waring et al., 1998). Oxygen 606 607 isotope ratios and particularly those of vein carbonate show stronger gradients between

mineralization zone and unaltered distal rocks and will therefore provide a clearer signal of thismineralization-related fluid flow (Fig. 11).

Classification of different vein generations based only on textural observations aided by 610 UV fluorescence studies is time-effective and provides an independent tool to distinguish 611 significant from unimportant and unrelated veins. Vein carbonate stable isotope ratios can be 612 combined with trace-element analysis (As, Fe, Mn, Zn, La, Ce, Pr, Sm, Eu, Gd) of select 613 614 samples to evaluate different vein types for their metal concentrations and constrain redox 615 conditions of the vein forming fluid. In addition, it is possible that portable XRF analysis of carbonate veins may be useful to help further characterize carbonate vein chemistry (Andrew and 616 Barker, 2017) and aid in identifying and discriminating vein generations. The method of isotopic 617 analysis employed here, incorporating sampling using a handheld drill followed by laser 618 spectrometry analysis represents an adequate approach to achieve the required sample throughput 619 620 rate in mineral exploration programs. The robustness and simple operation of available ICOS isotope analyzers are beneficial for this application and allow real-time stable isotope analyses 621 during core logging on site. Indeed, the low power and consumable requirements mean that the 622 analytical setup utilised for this study could be easily deployed in a core shed (or even in a fly 623 624 camp) setting if needed for rapid data turnaround.

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#### CONCLUSIONS

626 Formation of the Cinco de Mayo Zn-Ag deposit was accompanied by extensive stable isotope alteration of the host limestone formations. This alteration is best developed in the 627 Middle Albian Finlay Formation, which was the major aquifer for the hydrothermal 628 mineralization fluid. The stable isotope composition of pervasively altered holes intersecting the 629 Pegaso Zone mineralization indicates hydrothermal fluid flow also crossed formation boundaries 630 631 for ~200 m into the underlying Lagrima and Benigno Formations. Hydrothermal limestone alteration resulted in an overall shift of average wall rock stable isotope ratios to values lower 632 than in the least altered distal hole (CM09-94) as well as strongly erratic stable isotope ratios of 633 individual samples that vary up to 10% over depth intervals of 10 m and less. Based on 634 635 macroscopic textural observations of calcite veins and their stable isotope composition, three different vein generations can be identified, which represent fluid flow during limestone 636 diagenesis and during and after mineralization, respectively. The stable isotope composition of 637 syn-mineralization veins and their wall rocks is consistent with an advection-dominated reactive 638 flow model and isotope exchange during mineral dissolution-precipitation reactions driven by a 639 large flux of high-temperature magmatic fluid. The correlation of vein calcite trace-element 640 concentrations with stable isotope ratios corroborates their classification as pre-, syn-, and post-641 mineral fluid pathways. The highly variable limestone wall rock stable isotope composition in 642 the mineralization zone and the existence of wall rock samples that are isotopically depleted 643 644 relative to adjacent syn-mineralization veins imply that fluid flow was locally channelized and aided by brittle deformation. Overall, the lateral extent of detectable stable isotope alteration in 645

proximal and distal holes for up to 10.6 km away from the Pegaso Zone mineralization along 646 strike of the Finlay Formation defines the size of the stable isotope footprint of the Cinco de 647 Mayo Zn-Ag deposit. Combining this with zoning and variability of stable isotope results 648 indicates that stable isotope studies can aid mineral exploration programs: 1) By defining the 649 650 magnitude of the overall system, 2) As a vectoring tool and 3) To identify pathways preferentially followed by the hydrothermal fluids, which may also represent sites for metal 651 accumulation. An example of the practical application of these results is the strong indication that 652 additional exploration potential exists near proximal hole CM08-45 because its degree of stable 653 654 isotope alteration is comparable to mineralization zone samples. In addition, the lack of stable isotope ratio transition from altered to background values with depth in CM10–247 suggests that 655 alteration and perhaps mineralization extend to levels deeper than captured by exploration 656 drilling. 657

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#### **FIGURE CAPTIONS**

Fig. 1 Geological map of the Cinco de Mayo property showing the location of investigated drill
holes and surface projection of the Pegaso Zone and Pozo Seco Zone mineralization.

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**Fig. 2** Downhole O and C isotope ratios in wall rock and vein calcite samples from **(A)** the least altered hole (CM09–94) and **(B)** the mineralization zone (CM12–431). The brown dashed line represents the five–point moving average for wall rock  $\delta^{18}$ O and  $\delta^{13}$ C values. The bulk rock Ag concentration (ppm; secondary abscissa) is displayed as a proxy for mineralization.

**Fig. 3** Box plots for Finlay Formation (**A**) limestone wall rock and (**B**) G2 veins plotted in the order of increasing distance from CM12–431. CM12–431 was chosen as the origin based on the presence of hornfels, skarn and strong mineralization. CM10–247 intersects the Pozo Seco Zone mineralization and is plotted to the left of CM12–431. The span of the boxes represents the composition of 50% of the data population (interquartile range), the band within the box represents the median and the dot is the mean. The whisker length is 1.5 times the interquartile range; crosses define the 1% and 99% interval.

Fig. 4 Mosaic showing representative normal and UV light images of the different vein
generations in half core samples together with measured O and C isotope ratios. Note the yellow
color of vein carbonate in G2 veins in CM12–431 indicating the presence of ankerite.

**Fig. 5**  $\delta^{13}$ C vs  $\delta^{18}$ O data of the different calcite vein generations at Cinco de Mayo. Vein classification is based only on macroscopic textural observations but is consistent with distinct stable isotope compositions. Classification of G2a and G2b veins is based on cross-cutting relationships between veins that are both texturally consistent with generation 2 veins. G2b veins are always younger than G2a veins.

Fig. 6 PAAS-normalized vein calcite REE pattern from the three vein generations in
 mineralization zone, proximal and distal samples. REE concentrations are average values
 calculated from the concentration of several laser ablation spots in each vein type per sample.

**Fig. 7** Vein calcite Nd concentrations plotted against  $\delta^{18}$ O for the three vein generations in mineralization zone, proximal and distal samples. The spread in Nd concentrations reflects the per-vein compositional heterogeneity.

**Fig. 8** Box plots showing the spread in select trace metal concentrations and ratios plotted against vein calcite  $\delta^{18}$ O for the three vein generations in mineralization zone, proximal and distal holes.

**Fig. 9** Conceptual 1–dimensional model of fluid flow and stable isotope alteration in limestone during infiltration of magmatic fluid. The composition of altered wall rock (solid lines) and coexisting veins (stippled lines) are shown for different Damköhler and Peclet numbers. The input fluid  $\delta^{18}$ O composition (9‰) is consistent with a magmatic fluid, the initial wall rock  $\delta^{18}$ O

- composition represents the stable isotope background (22.5%) in CM09–94. Fluid transport is 697 from left to right. The fluid-calcite oxygen isotope fractionation factor (Chacko et al., 2001) is 698 calculated for an assumed temperature of 360 °C (see text for discussion). (A) Wall rock and vein 699  $\delta^{18}$ O composition as a function of distance from the fluid inlet, showing the shape of the 700 701 alteration front in wall rock and vein samples for different fluid transport scenarios. (B) Compositional difference between wall rock and vein (2180WR-vein) for the fluid transport 702 scenarios shown in (A) as a function of distance from the fluid inlet. (C)  $\Delta^{18}O_{WR-vein}$  plotted 703 against  $\delta^{18}O_{WR}$  for the different cases shown in (A) and (B). 704
- Fig. 10  $\Delta^{18}O_{WR-vein}$  vs.  $\delta^{18}O_{WR}$  values of mineralization zone, proximal and distal samples. (A) All data including negative  $\Delta^{18}O_{WR-vein}$  values representing incomplete wall rock alteration (see text for discussion). (B)  $\Delta^{18}O_{WR-vein}$  vs.  $\delta^{18}O_{WR}$  pairs shown for  $\Delta^{18}O_{WR-vein} > 0$  using G2 veins from the Finlay Formation only. The contour lines represent distance–normalized time– integrated fluid flux (stippled lines; z/TIFF) and Damköhler numbers (solid lines; N<sub>D</sub>). Compare with Figure 9C for the construction of the contour lines.

Fig. 11 Box plot showing the  $\delta^{18}$ O and  $\delta^{13}$ C composition of (A) Finlay wall rock and (B) vein samples plotted as function of distance from CM12–431. The solid (wall rock) and stippled (vein) lines in  $\delta^{18}$ O plots represent the best fit of the real data to the 1–dimensional transport model shown in Fig. 9 using advection dominated fluid flow (N<sub>Pe</sub> = 100) and Damköhler numbers of 1.5 and 5.

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Figure 1





#### A) Finlay wall rock























Figure 10



### A) Finlay wall rock











Formation	Age	Description	Thickness
Benavides	Late Albian	Medium gray, argillaceous limestone to variably fossiliferous and calcareous shale sequence. Indicative alternation of dark gray calcareous shale with light gray micritic limestone on the tens of meter scale.	~300–400 m
Finlay	Middle Albian	Medium gray carbonate with variable fossil content and black chert. Carbonate ranges from micrite to sparite and calcarenites. The upper 20 m sometimes contain a storm rip up clast horizon producing permeability and is frequently characterized by hematite stained solution cavities, coarse white calcite, and chalcedony–quartz deposits. This zone as well as the upper and lower stratigraphic contacts are the main loci for mineralization.	~100–200 m
Lagrima	Middle Albian	Black calcareous shale to dark gray, variably fossiliferous argillaceous limestone. The black shale dominates in drill core and frequently contains thin beds of limestone.	~ 30–100 m
Benigno	Early Albian	Medium gray carbonate with variable fossil content, variable black chert and minor shale partings. Within the district, the Benigno fomation is capped by a very distinctive, strongly bioturbated carbonate mud transition zone from the Lagrima Formation. The carbonate ranges from micrite to sparite displaying a rich biotic carbonate mud supported reef environment.	~ 200–300 m
Cuchillo	Aptian	Alternating 1 to 20 meter thick limestone beds interbedded with calcareous black shale of equal thinkesses.	> 500 m

 Table 1 Summary and description of limestone formations at Cinco de Mayo.

		enavides		Lagrima				Benigno					Cuchillo							
	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n
CM09-94 WR	3.12	0.62	22.26	1.77	31	3.19	0.87	22.34	2.44	14										
CM09-94 veins	2.66	1.11	21.10	2.25	19	3.01	0.85	18.01	2.78	15										
CM09-88 WR											2.81	1.66	22.01	1.31	19	2.66	1.14	18.19	2.35	12
CM09-88 veins											0.16	4.29	19.37	2.83	12	1.28	0.82	16.66	2.42	9
CM09-89 WR						2.51	0.42	20.49	1.22	9	3.65	0.51	20.99	1.53	36	3.42	0.56	20.82	1.60	32
CM09-89 veins						1.73	0.36	18.74	0.96	3	3.23	1.48	20.58	1.46	22	3.26	0.81	20.48	1.44	23
CM09-127 WR	2.14	0.72	19.01	1.61	5	2.74	0.47	15.52	1.55	3	2.43	0.28	20.34	0.40	4					
CM09-127 veins	1.30	1.80	17.23	2.14	4	1.85	0.61	16.83	2.06	3										
CM10-292 WR						1.61	2.25	21.65	6.17	2	2.48	0.57	22.49	3.19	3					
CM10-292 veins						2.05	0.98	15.49	11.86	2	1.40	0.90	20.26	0.56	2					
CM10-305 WR						3.89		17.82		1										
CM10-305 veins						3.55		9.72		1										
CM11-380 WR						3.05	0.44	17.86	2.91	7										
CM11-380 veins						1.48	1.45	17.07	3.22	8										
CM12-423 WR						2.01	1.24	18.54	1.79	16	2.30	0.54	21.77	1.60	18					
CM12-423 veins						0.73	0.59	16.04	2.06	12	1.88	0.80	21.29	5.06	3					
CM12-431 WR	1.77	0.96	14.65	1.63	12						2.69	1.06	20.94	2.30	30					
CM12-431 veins	-0.37	1.19	14.32	0.70	14						1.83	1.19	13.22	3.02	3					
CM10-247 WR						1.83	1.07	14.44	0.98	7	2.60	1.05	15.99	2.02	35	2.96	0.55	14.42	1.04	7
CM10-247 veins						0.17	2.00	17.32	0.98	5	1.65	1.20	15.17	5.27	27	1.96	0.81	15.87	2.44	13

**Table 2** Average carbon and oxygen isotope composition of limestone wall rock (WR) and vein samples outside of the Finlay Formation. The standard deviation  $(1\sigma)$  reflects the spread of the overall data population.

		Wa	all rock								
Core ID	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n	$\delta^{13}$ C (‰, VPDB)	s.d. $\delta^{13}$ C	$\delta^{18}$ O (‰, VSMOW)	s.d. $\delta^{18}$ O	n	Distance from CM12-431 (km)
Distal cores											
CM09-94	2.89	0.63	22.45	1.29	27	3.36	0.96	21.66	2.26	17	12.7
CM09-88	Finlay Formation not present in CM09-88										11.1
CM09-89	2.85	0.80	22.94	2.26	11	2.78	1.34	21.00	0.71	7	10.6
Proximal cores											
CM09-127	3.71	0.23	19.52	0.55	4	2.91	0.48	18.61	0.32	2	10.1
CM10-292	2.23	1.13	18.73	2.00	10	1.91	1.06	14.82	2.51	5	7.8
CM10-305	1.39	2.22	18.94	2.11	29	0.73	2.49	18.04	0.74	5	6.9
CM10-317	1.25 2.09 20.76		1.25	13	No		5.9				
CM10-332	0.96	1.17	15.51	2.92	9	2.45	0.55	11.90	1.48	9	4.5
CM08-45	1.08	1.33	16.61	2.06	15	1.05	1.57	16.43	2.44	9	4.1
CM06-01	1.74	2.04	17.88	2.46	13	-0.23	2.72	16.89	1.49	6	1.8
Mineralization ze	one cores										
Pegaso Zone	mineralizat	ion									
CM07-20	2.10	1.60	15.57	2.54	3	0.96	1.89	15.91	2.04	3	1.4
CM11-380	2.56	0.95	17.44	3.21	27	-0.83	1.36	12.94	2.69	13	1.0
CM12-423	1.87	1.16	19.62	2.21	49	0.37	0.78	15.89	1.30	13	0.3
CM12-428	1.88	0.87	17.20	3.85	6	0.31	1.28	16.51	1.67	5	0.3
CM12-431	1.78	1.17	17.18	2.69	43	-0.84	1.86	13.90	3.22	21	0.0
Pozo Seco Zo	ne minerali	zation									
CM10-247	2.47	0.74	14.48	1.35	25	-0.53	1.12	13.19	1.45	8	6.0

**Table 3** Average carbon and oxygen isotope composition of Finlay limestone wall rock and G2 vein samples. The standard deviation  $(1\sigma)$  reflects the spread of the overall data population.

Hole ID	CM09-94		CM11-380		CM06-01		CM0e	5-01	CM0	5-01	CM0	6-01	JM12-423	
Vein type	G2		G	2	G	1	G	1	G	2	G	2	G	1
$\delta^{13}$ C (‰)	3.0 ±	0.5	$-2.0 \pm 0.5$		2.6 ±	0.8	2.1 ±	0.8	1.4 ±	$1.4 \pm 0.8$		$-1.4 \pm 0.8$		± 0.8
$\delta^{18}$ O (‰)	$21.3 \pm 0.8$		$10.8\pm0.7$		$17.1\pm0.2$		$18.2\pm0.1$		$19.0\pm0.1$		$15.0 \pm 0.1$		$23.5\pm0.1$	
n	6		2		2		2		2		3		4	
	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.
Mg	33.3	9.15	78.6	45.4	31.3	1.28	37.0	0.877	32.0	5.30	28.0	10.5	163	12.4
Si	14.5	2.38	13.2	2.40	15.5	0.495	12.8	1.13	12.3	0.283	28.5	22.1	9.70	1.28
Р	0.220	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.670	0.255	0.362	b.d.l.	b.d.l.	b.d.l.
S	1.96	0.204	4.00	0.297	2.73	0.417	2.57	0.148	27.1	2.41	8.32	5.49	3.33	0.430
Mn	5.06	0.424	167	57.9	10.6	3.96	17.9	19.7	25.8	3.16	82.9	46.6	2.21	0.196
Fe	30.4	15.8	187	16.0	4.52	0.905	9.85	10.4	83.8	7.00	87.8	28.3	4.94	1.50
Cu	0.008	0.009	0.002	0.000	0.004	0.001	0.003	b.d.l.	0.018	b.d.l.	0.005	0.003	0.005	0.003
Zn	0.050	0.015	0.050	0.028	0.043	0.007	0.113	0.052	0.068	0.034	0.143	0.169	0.024	0.007
As	0.017	0.012	0.012	0.001	0.015	0.006	0.011	0.002	0.011	0.004	0.011	0.001	0.009	0.002
Sr	4.04	0.608	13.3	5.73	9.23	5.18	6.73	0.278	9.06	5.08	9.09	1.95	12.9	0.219
Y	0.039	0.005	0.037	0.047	0.013	0.013	0.016	0.021	0.010	0.002	0.129	0.054	0.020	0.007
Ва	0.016	0.004	0.022	0.008	0.028	0.010	0.022	0.012	0.013	0.014	0.268	0.418	0.010	0.002
La	0.056	0.108	0.022	0.013	0.015	0.013	0.024	0.033	b.d.l.	b.d.l.	0.246	0.175	0.019	0.005
Ce	0.110	0.208	0.036	0.031	0.026	0.027	0.041	0.053	b.d.l.	b.d.l.	0.334	0.225	0.041	0.010
Pr	0.012	0.022	0.005	0.005	0.003	0.003	0.009	b.d.l.	b.d.l.	b.d.l.	0.037	0.024	0.005	0.002
Nd	0.065	0.118	0.024	0.023	0.016	0.018	0.025	0.033	b.d.l.	b.d.l.	0.198	0.134	0.027	0.007
Sm	0.006	0.007	0.012	b.d.l.	0.005	b.d.l.	0.009	b.d.l.	b.d.l.	b.d.l.	0.036	0.023	0.005	0.002
Eu	0.001	0.001	0.005	0.005	0.002	0.000	0.009	b.d.l.	b.d.l.	b.d.l.	0.040	0.047	0.001	0.000
Gd	0.007	0.004	0.014	b.d.l.	0.005	b.d.l.	0.013	b.d.l.	b.d.l.	b.d.l.	0.038	0.024	0.005	0.002
Tb	0.001	0.000	0.003	b.d.l.	0.001	b.d.l.	0.001	b.d.l.	b.d.l.	b.d.l.	0.005	0.003	0.001	0.000
Dy	0.006	0.001	0.011	b.d.l.	0.002	0.002	0.007	b.d.l.	b.d.l.	b.d.l.	0.023	0.012	0.003	0.001
Но	0.001	0.000	0.001	0.001	0.001	b.d.l.	0.001	b.d.l.	b.d.l.	b.d.l.	0.004	0.002	0.001	0.000
Er	0.003	0.001	0.003	b.d.l.	0.002	b.d.l.	0.002	b.d.l.	b.d.l.	b.d.l.	0.007	0.003	0.002	0.001
Tm	0.000	0.000	0.000	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.001	0.000	0.000	0.000
Yb	0.003	0.000	0.001	b.d.l.	0.002	b.d.l.	0.002	b.d.l.	0.000	b.d.l.	0.004	0.002	0.002	b.d.l.
Hf	0.001	0.001	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.001	b.d.l.	b.d.l.	b.d.l.
Tl	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.1.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	0.002	0.001	0.016	0.007	0.005	0.000	0.008	0.006	0.003	0.002	0.048	0.069	0.025	0.024
Th	0.000	0.001	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.001	0.002	b.d.l.	b.d.l.
U	0.002	0.003	0.002	0.001	0.000	b.d.l.	0.000	0.000	0.001	b.d.l.	0.003	0.003	0.002	0.003

Table 4 Average trace-element concentrations in Finlay calcite veins from the mineralization zone, proximal and distal holes together with their stable isotope composition.

b.d.l. = below the detection limit.  $\delta^{13}$ C relative to VPDB,  $\delta^{18}$ O relative to VSMOW. The standard deviation (1 $\sigma$ ) reflects the spread of the overall data population.

Table 4 cor	ntinued.													
Hole ID	JM12-423		JM12-423 CM12-431			2-431	CM12	2-431	CM12	2-431	CM10	-247	CM10	)-247
Vein type	e G2		G1		G2		G	G2		3	G2		G2	
$\delta^{13}$ C (‰)	$0.7 \pm 0.8$		$0.1 \pm 0.2$		$-0.6 \pm 0.2$		$0.3 \pm 0.2$		-1.5 ±	- 0.1	1.8 ±	0.8	-0.5 ±	± 0.3
$\delta^{18}$ O (‰)	15.5 ±	15.5 ± 0.1 20.4		$20.5 \pm 0.4$		$13.3\pm0.4$		$14.2 \pm 0.4$		± 0.4	16.5	± 0.1	13.8 ± 0.4 4	
n	3		3 7		7		5		6		3			
	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.	avg ppm	s.d.
Mg	2356	200	81.8	7.63	79.5	74.8	1585	1026	182	65.6	41.0	7.41	56.1	9.25
Si	17.7	3.50	22.8	12.0	125	173	23.7	2.66	13.8	1.90	15.1	0.635	14.1	1.75
Р	b.d.l.	b.d.l.	b.d.l.	b.d.l.	22.7	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.298	0.027	b.d.l.	b.d.l.
S	3.68	0.171	2.34	0.932	3.85	3.26	1.51	0.214	5.84	1.11	3.87	1.64	2.13	0.084
Mn	813	44.4	2.66	0.559	72.5	54.5	576	272	136	17.5	1.27	0.235	106	6.47
Fe	2846	318	2.99	0.390	259	201	2394	1579	383	98.0	2.50	1.15	203	24.1
Cu	0.007	0.001	0.006	0.002	0.102	0.134	0.075	0.124	0.022	0.036	0.004	0.001	0.005	0.002
Zn	0.252	0.008	0.030	0.011	b.d.l.	b.d.l.	0.412	0.284	0.084	0.033	0.060	0.006	0.044	0.010
As	0.021	0.004	0.014	0.004	0.043	0.031	0.008	b.d.l.	0.030	0.013	0.013	0.003	0.008	0.001
Sr	9.14	0.320	11.9	0.623	10.6	2.18	8.68	2.16	12.0	0.584	9.95	3.38	7.73	0.230
Y	0.036	0.010	0.006	0.003	0.529	0.695	0.556	0.201	0.078	0.047	0.019	0.024	0.000	0.000
Ba	0.096	0.005	0.022	0.016	0.048	0.038	0.058	0.016	0.048	0.017	0.021	0.005	0.013	0.008
La	0.093	0.025	0.016	0.007	0.818	1.47	0.340	0.159	0.445	0.178	0.006	0.007	0.002	0.001
Ce	0.125	0.035	0.030	0.011	1.44	2.55	0.724	0.307	0.413	0.219	0.009	0.012	0.002	0.001
Pr	0.013	0.004	0.003	0.001	0.162	0.283	0.092	0.035	0.037	0.021	0.001	0.002	0.000	b.d.l.
Nd	0.069	0.018	0.017	0.006	0.852	1.49	0.472	0.170	0.204	0.112	0.009	0.010	0.001	0.000
Sm	0.008	0.001	0.002	0.001	0.151	0.265	0.100	0.031	0.025	0.016	0.002	0.002	0.000	0.000
Eu	0.011	0.002	0.001	0.000	0.053	0.091	0.041	0.010	0.060	0.013	0.001	0.000	0.000	0.000
Gd	0.008	0.002	b.d.l.	b.d.l.	0.155	0.270	0.108	0.041	0.023	0.016	0.006	b.d.l.	b.d.l.	b.d.l.
Tb	0.001	0.000	b.d.l.	b.d.l.	0.020	0.030	0.017	0.007	0.003	0.001	0.001	b.d.l.	b.d.l.	b.d.l.
Dy	0.005	0.001	0.002	0.001	0.093	0.121	0.097	0.036	0.012	0.008	0.006	b.d.l.	b.d.l.	b.d.l.
Но	0.001	0.000	0.000	0.000	0.015	0.019	0.018	0.006	0.002	0.001	0.000	0.001	b.d.l.	b.d.l.
Er	0.002	0.000	0.001	b.d.l.	0.034	0.042	0.037	0.011	0.005	0.003	0.002	0.001	b.d.l.	b.d.l.
Tm	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.004	0.005	0.004	0.001	0.001	0.000	0.000	b.d.l.	b.d.l.	b.d.l.
Yb	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.024	0.032	0.019	0.004	0.002	0.002	0.001	b.d.l.	b.d.l.	b.d.l.
Hf	b.d.1.	b.d.l.	b.d.l.	b.d.l.	0.013	0.010	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.001	0.000	0.000	b.d.l.
T1	b.d.l.	b.d.l.	0.002	0.001	0.001	0.001	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	0.017	0.006	0.010	0.001	0.044	0.043	0.025	0.006	0.023	0.004	0.003	0.000	0.016	0.000
Th	0.000	0.000	b.d.l.	b.d.l.	0.014	0.014	0.001	0.000	0.000	0.000	0.001	0.001	b.d.l.	b.d.l.
U	0.002	0.001	b.d.l.	b.d.l.	0.046	0.062	0.000	0.000	0.001	0.000	0.123	0.103	b.d.l.	b.d.l.

b.d.l. = below the detection limit.  $\delta^{13}$ C relative to VPDB,  $\delta^{18}$ O relative to VSMOW. The standard deviation (1 $\sigma$ ) reflects the spread of the overall data population.