ALBERTA INNOVATES

CLEAN RESOURCES FINAL REPORT PACKAGE

Project proponents are required to submit a Final Report Package, consisting of a Final Public Report and a Final Financial Report. These reports are to be provided under separate cover at the conclusion of projects for review and approval by Alberta Innovates (AI) Clean Resources Division. Proponents will use the two templates that follow to report key results and outcomes achieved during the project and financial details. The information requested in the templates should be considered the minimum necessary to meet AI reporting requirements; proponents are highly encouraged to include other information that may provide additional value, including more detailed appendices. Proponents must work with the AI Project Advisor during preparation of the Final Report Package to ensure submissions are of the highest possible quality and thus reduce the time and effort necessary to address issues that may emerge through the review and approval process.

Final Public Report

The Final Public Report shall outline what the project achieved and provide conclusions and recommendations for further research inquiry or technology development, together with an overview of the performance of the project in terms of process, output, outcomes and impact measures. The report must delineate all project knowledge and/or technology developed and must be in sufficient detail to permit readers to use or adapt the results for research and analysis purposes and to understand how conclusions were arrived at. It is incumbent upon the proponent to ensure that the Final Public Report **is free of any confidential information or intellectual property requiring protection**. The Final Public Report will be released by Alberta Innovates after the confidentiality period has expired as described in the Investment Agreement.

Final Financial Report

The Final Financial Report shall provide complete and accurate accounting of all project expenditures and contributions over the life of the project pertaining to Alberta Innovates, the proponent, and any project partners. The Final Financial Report will not be publicly released.

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Mapping potential point sources impacting Alberta's groundwater by the migration of gas from oil and gas well sites**
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AI Project Advisor:	Mark Donner

2. APPLICANT INFORMATION:

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A. EXECUTIVE SUMMARY

The main objective of this project was to identify aquifers in Alberta that may have been impacted by many hundreds of thousands of energy wells drilled over the last century. The method was to compare on a regional scale the isotopic composition of free hydrocarbon gases evolving from domestic water wells to both fugitive and production gases from nearby hydrocarbon resource wells in Alberta. We contour mapped and profiled the carbon isotopic composition of free hydrocarbon gases from 1124 domestic water wells across Alberta. Most but not all of the water well data are from central Alberta sampled as part of the Coalbed Methane (CBM) baseline water well initiative. We prepared separate detailed isotope contour maps and profiles in central Alberta, where we had the highest density of water well analyses, as well as numerous samples of ground migration (soil gases), surface casing vent (SCV), flows and production gases. It is well known that in Alberta many domestic water wells release methane, which is often attributed to localized biogenic processes, i.e. "swamp gas". However, deeper thermogenic gases (propane and butanes) were recorded in 6 to 9% of the sampled water wells. We compared the regional variations of the isotopic composition of the domestic water well gases to coincident contour maps of ground migration and surface casing vent flow gases of energy wells recorded in the University of Alberta gas isotope database. Regional maps of hydrocarbon gases stable isotopic composition maps measured in domestic water wells show several specific regions where such wells contain thermogenic gases, requiring further detailed hydrogeological and hydrogeochemical investigation.

In central Alberta, the isotopic contour maps and profiles for methane and ethane from domestic water wells display complex geographic patterns that reflect topography to some extent. In specific regions (on a kilometer-scale) the isotopic variations and the presence of propane and butanes in domestic water wells cannot be explained by biogenic processes alone but require admixture of deeper thermogenic gas. Inspection and comparison of the domestic water well maps and profiles to ground migration (GM) and surface casing vent (SCV) gases from the same locations reveal some similarities and parallelism. Hence, suggesting thermogenic fugitive gases migrating from energy wells may have locally impacted the aquifers. Further detailed work is necessary to identify the source of this thermogenic gas. The apparent link of the isotope composition of the water well methane, not impacted by deep thermogenic gas, to topography, implies that methane is evolving in flowing aquifers. Yet, our study needs to be placed in the context of regional hydrogeology, hydrogeochemistry and geology.

B. INTRODUCTION

Flammable hydrocarbon gas in domestic water wells in Alberta and elsewhere has been a contentious topic. The origin of the gases is debated as either natural, from shallow biogenic sources, if of deep origin, migrating along with preexisting fractures or faults, or having escaped from nearby faulty resource wells. Public controversy led the EUB to mandate baseline water well testing of domestic water wells in prospective Coalbed Methane (CBM) targeted regions (e.g. Ryan, 2009). The mandate required carbon isotopic analyses of any free hydrocarbon gases found in a large subset of domestic water wells. In principle, the carbon isotope fingerprint of the gas should identify its origin. In 1999 the then Alberta Regulator recognized carbon isotope fingerprinting (EUB, GB 99-6, 1999) as a useful tool, developed at Prof. Muehlenbachs' laboratory facilities, to identify source depths of migrating gases from oil and gas wells. Since then, many thousands of ground migrating (GM) and surface casing vent (SCV) flow gases have been analyzed at the University of Alberta. With funding from the Petroleum Technology Alliance of Canada (PTAC), our group has contour mapped the variation of carbon isotope values measured in natural gases across the Western Canada Sedimentary Basin (WCSB). A new value-added finding from mapping GM and SCVF isotope data over topography evidenced enigmatic relationships between topography and fugitive gases' source depth.

Experience has shown that most GM and SCVF fugitive gases entering the environment do not originate from the production targets, but emanate from shallower formations along the wellbore. In any given area, most leaks come from certain Formations. An obvious next step is to map and compare the isotopic variations recorded for free gases in domestic water wells to the known isotopic variations in fugitive and production gases from nearby energy wells.

The science causing the variations of isotope compositions that we have contour mapped is relatively simple and well known. The ratio of the stable carbon isotopes, ^{13}C to ^{12}C, in a substance is fractionated a little by physical, chemical and biological processes. The size of the partitioning depends on temperature. Largest effects occur at lowest temperatures, the smallest at a higher temperatures. Gases show the largest effects, solids and liquids relatively small effects. Among gases, the largest effect is with the lowest molecular weight moieties, namely methane and the smallest effect among the heaviest molecules, ethane, propane and butane, in that order (Chung *et al*., 1988). Thus shallow biogenic methane will have the greatest partitioning and be the most depleted in ^{13}C, and therefore, most negative delta values (approximately -65‰ for biogenic gases)(Whiticar, 1999). When hydrocarbons are oxidized in shallower, oxygenated waters, the ^{12}C molecules are selectively lost first such that the residual methane becomes enriched in ^{13}C with its delta value becoming less negative (even as high as -20 or -30‰) balanced by a decrease in ^{13}C of dissolved CO_2.

In a classic "oil window" scenario, where the source kerogen is more or less uniform, one can predict that shallow gases formed at lower maturities (Rowe and Muehlenbachs, 1999). This will reflect the largest isotope fractionations (methane values of -55 to -50‰), but at the peak of the "oil window" around -46‰, whereas the deepest mature and overmature gases have methanes in the -25 to -35‰ range. Simultaneously, the isotopic differences (fractionations) between methane, ethane and propane will decrease with maturity in proportion to their molecular weights such that methane always should contain the least ^{13}C, butane the most (Chung *et al*., 1988). However, such an ideal case is very rarely observed in nature (e.g. Milkov *et al*., 2020). Overmature, deep shale gases show unexpected isotope patterns between methane and heavier hydrocarbons. Microbiological or abiological alteration can selectively alter the hydrocarbon gases' carbon isotope ratio, as will the mixing of gases from different sources. The net result in natural systems is that the carbon isotope ratio of natural gases varies across a petroliferous basin in a complicated but understandable way (see Fig. 1 from Tilley and Muehlenabchs, 2006). In aquifers mixing shallow, in situ bacterially generated gas with deeper thermogenic gases is expected. Such expected intricacies in the isotope geochemistry will be shown in various geochemical cross plots later in this report.

C. PROJECT DESCRIPTION

The utility of stable isotope analyses to identify the source of natural gases in waters is well documented and not at all controversial, but has been precluded in many practical field situations for lack of baseline data (i.e. knowing the isotopic composition of putative end-members of gases in a complex mixed gas system). To remedy this deficiency, the then regulator, EUB, mandated that prior to any CBM drilling, operators had to isotopically fingerprint any hydrocarbon gas if present in a subset of domestic water wells within 600 m radius of a proposed CBM well. These analyses are the core of this report. But, it should be noted that in that same CBM targeted area in central Alberta, before the sampling of the water wells, at least 70,000 energy wells were drilled targeting deeper conventional oil and gas reservoirs. This raises questions of what a baseline truly is. This study maps and documents the regional variation of the stable carbon isotopic composition of single hydrocarbon gas moieties in Alberta's domestic water wells. These values were compared to known fugitive gases emanating from energy wells in the same region and test the extent to which faulty energy wells may have impacted regional aquifers.

D. METHODOLOGY

Data analysis, compilation and mapping

The carbon isotope values of *n*-alkane and carbon dioxide gases are presented for 1124 water wells across the basin (Fig. 1). Figs. 2, 3 & 4 show the location of samples of ground migration, surface casing vent flow and production gases to which we will compare the domestic water well data. Data were taken from the University of Alberta database, organized, formatted and mapped. All the methane ($\delta^{13}C_1$, ‰, VPDB), ethane ($\delta^{13}C_2$, ‰, VPDB), propane ($\delta^{13}C_3$, ‰, VPDB), n-butane ($\delta^{13}nC_4$, ‰, VPDB), iso-butane ($\delta^{13}iC_4$, ‰, VPDB), as well as carbon dioxide ($\delta^{13}CO_2$, ‰, VPDB) data, were acquired using a Finnigan-MAT 252 GC-CF-IR MS at the University of Alberta (see for details Tilley and Muehlenbachs, 2012). Descriptive statistics have been performed for the domestic water wells measurements to understand the variables' general distribution (Fig. 5, e.g. boxplot, and mean values).

A kriging model was used to map the gas isotope data (Pyrcz and Deutsch, 2014). Interpolation via simple kriging produces maps that are too smooth by their very nature: best estimates will never reproduce values at the tail ends of the input distributions (extreme highs and lows). However, such isoscapes aid at predicting potential isotopic responses. Regional contour maps of methane, ethane and carbon dioxide isotope values were generated for water wells (WW–Figs. 6, 8 & 9) and production oil associated gas (Figs. 20 to 24), (GM–Figs. 12 & 14); surface casing vent (SCV–Figs. 16 & 18). These contour maps are draped over topography for WW (Figs. 7, 9 and 11); GM (Figs. 12 and 15); SCV (Figs. 17 and 19); and production (Figs. 21, 23 and 25).

E. PROJECT RESULTS

Regional data source and interpretation

Our sample locations are shown in Fig. 1 for domestic water wells, Ground migration (GM) Fig. 2, surface casing vent flow (SCV) Fig. 3, production gas Fig. 4. The nature of each substrate, and gas sample sources, were defined as follows:

Water wells (WW): free gas samples collected from domestic water wells as mandated by the EUB for the Baseline Water Well Testing Program (EUB GB 99-6, 1999). Gas samples from the domestic water wells were collected by various companies following a variety of procedures.

Ground Migration (GM): gas sampled from the ground or soil adjacent to an energy well. Also called soil gas, which is gas spreading from flaws and failures in the energy well often mixed and degraded within the vadose zone—samples collected by industry at various shallow depths and roughly a meter or less from the energy well.

Surface Casing Vent (SCV): is gas from the surface casing/casing annulus of an energy well (often referred to as internal migration). By regulation, SCVs are left open and vent to the atmosphere. It is part of surface gas leakage that leads to direct emission of gases to the atmosphere and surroundings and is usually related to the well’s infrastructure distribution, or casing failure. The prevalence of SCV from wells varies due to location, age, etc. but is perhaps found in 10 to 20% of cases. Samples collected by industry.

Production Gas: natural gas sampled from well separator or meter run. The sample represents an aliquot of *n*-alkanes from the targeted reservoir. It is important to note that our reported “production” gases are both oil-associated gases and commercially produced natural gas. Samples collected by industry.

Isotopic composition of domestic water well (WW) gas

In total, we compiled the gas isotopic composition of 1124 domestic water wells. Figure 5 shows the isotopic composition of methane, ethane, propane, butanes and carbon dioxide of all sampled domestic water wells. Methane isotopic composition values vary from -98.07‰ to -19.23‰, mean value -65.08‰ and standard deviation of ±10.26‰. Of note is that Humez *et al*. (2016) observed the same wide range and standard deviation in methane values in observation wells across Alberta. Ethane values range between -74.74‰ to -7.54‰, mean value -48.24‰ and standard deviation of ±7.38‰; propane values are from -58.65‰ to -12.9‰, mean value -31.63‰ and standard deviation of ±7.52‰ ; *iso*-butane isotopic composition showed a narrower distribution from -36.77‰ to -11.08‰, mean value -28.24‰ and standard deviation of ±3.24‰; *n*-butane values range from -38.41‰ and -19.5‰, mean value -28.44‰ and standard deviation of ±3.63‰; and carbon dioxide values showed a broadest distribution from -88.59‰ to +15.46‰, mean value -23.36‰ and standard deviation of ±13.09‰ (Fig. 5a).

Methane isotopic values lower than -55‰, suggest a shallow biogenic origin and are found in 88% of tested domestic water wells in agreement with data reported from observation wells of Alberta (e.g. Humez *et al*., 2016a,b). Heavier methane values, higher than -54‰ and up to -35‰, were reported in 8% of the samples, perhaps of thermogenic origin, while very enriched values more positive than -30‰ were reported in only 2% of the tested WW potentially linked to deep shale gas. However, enriched residual methane may result from bacterial methane oxidation in situ, or low concentration methane in sampling containers (Barker and Fritz, 1981a,b; Humez *et al*., 2016). Quality control advised by Humez *et al*., (2016) for sampling of water wells is to sample concentrations greater than 1500 ppmv and adequate sampling containers. Our study is based on all the available water well data on supersaturated free gas from domestic water taps. Thus, the gas was available in large volumes and usually high in hydrocarbon content, minimizing sampling and analytical error. Ethane isotopic analyses were reported in 77% of the samples, propane in 10% and butanes in only 6% of the domestic water wells. A few very negative ethane and propane values reported here, less than -50‰, may have different sources either as incipient, low-temperature thermogenic gas (Rowe and Muehlenbachs, 1999) or biodegradation related secondary gas (e.g. Larter *et al*., 2003) or, and less likely microbially produced ethane as well as light propane gas production (Taylor *et al*., 2000; Hinrichs *et al*., 2006). However, of the 77% wells showing ethane, only 3% showed ethane values higher than -34‰ along with propane (116 out of 118 samples). The enriched carbon isotope values in ethane and propane and the unusual presence of butanes in the water samples can be attributed to thermogenic gases. The observed carbon isotopic compositions of the propane and butanes overlap production gas values previously reported in the area (e.g. Tilley and Muehlenbachs, 2011; Tilley and Muehlenbachs, 2013) and will be discussed later in this report. The location of putative thermogenic gas in domestic water wells can be examined on the isoscape contour maps of methane, ethane and carbon dioxide. Visual comparison of the free gas in water can then be made with similar isotope contour maps of ground migration, SCVF and production gases. Most of the sampled domestic water wells are in central Alberta, and that region deserves a separate, closer study.

Mapping

Western Canada Sedimentary Basin (WCSB)

Fig. 6 is a colour-coded contour map of methane carbon isotope values from domestic water wells in the whole of the Western Canada Sedimentary Basin (WCSB). The warmer colors represent deeper sourced gas, whereas cold colors represent shallower gases. In Fig. 7, we drape the color contours over topography. Similarly, for ethane from domestic water wells, Fig. 8 & 9 and exsolved carbon dioxide Figs 10 & 11. Analogous maps for ground migration are given in Figs. 12 to 15 and for surface casing vent on Figs. 15 to 19 whereas production gas isotope data is mapped on Figs. 20 to 25. Cursory examinations of these maps reveal regional and local isotopic variations most easily visualized on production gas maps Figs. 20 to 25. The WCSB dips towards the west, where deeper reservoirs are exploited for more mature gases that are enriched in ^{13}C, reaching an extremum in the overmature Horn River play in NE BC (Tilley and Muehlenbachs, 2013). In contrast, remarkably low ^{13}C ethane is produced in the southeast, where gases produced from the Milk River, Medicine Hat and Second White Speckled Shale Formations are biogenic with an admixture of incipient thermogenic gas (Rowe and Muehlenabchs, 1999).

The contour maps of ground migration (Figs. 12 to 16) and surface casing vent flow (Figs. 17 to 19) follow overall the geographic trends seen in the production gases but differ significantly in detail. Over the whole basin, most leaking and migrating gas does not come from the targeted reservoirs, but is sourced somewhere shallower along the well bore (comparatively lower ^{13}C in gas). In the case of ground migration (GM), particularly methane, depending on the season, were oxidized to carbon dioxide leaving methane prone to more ^{13}C balanced by less ^{13}C in the CO_2. Recently, Muehlenbachs and Gonzalez Arismendi, (2021 –in review) documented that the isotopic composition of SCV (somewhat less pronounced with GM) in a given region was uniform, thus implying that most of the leaks were sourced from the same interval but that the source depth was often varied with topography.

The contour maps of domestic water wells (Fig. 6 to 11) show geographic patterns. Still, large patterns may be artifacts of model interpolations, except for central Alberta, because few domestic water wells were tested. Geographic patterns in central Alberta are real responses, and will be investigated in further detail.

Zoomed area

The distribution of sampled domestic water wells is biased. This report focuses on the region with the highest density of water wells (744) in central Alberta, from Range 11 W4 to Range 6 W5, and Townships (T) from 20 to 53 (Fig. 26). The chosen region also includes 71 examples of ground migration, 398 surface casing vents that also are also shown on Fig. 26 and 150 production gases (not shown in Fig. 26). At least 70,000 energy wells have been drilled in that area.

Figs. 27a & 27b show histograms of the isotopic composition of *n*-alkanes and carbon dioxide of the domestic water wells (WW), ground migration (GM), and surface casing vent (SCV) flows sampled in the zoomed area. Figure 27a shows the distribution for methane (Fig. 27aa), ethane (Fig. 27ab), and propane (Fig. 27ac). By comparing the three histograms, cut-off isotopic values per moieties were identified, thus separating the distribution and sample population. These values are: -62‰ for methane (a); -44‰ for ethane (b); and -35‰ for propane (c).

Methane shows a unimodal distribution for domestic water wells, ground migration, and displacement towards lighter methane values between -80 and -55‰. Both substrates overlap with surface casing vent flow. However, SCV may have a slightly bimodal distribution following the cut-off value for methane, with enricher methane values more than -60‰. A small number of samples, WW (n=41), GM (n=6), and SCV (n=10) overlap showing enriched methane values from -40.03‰ to -13.82‰.

Similarly, ethane values display a unimodal overlapping distribution for WW and GM (Fig. 27ab). Both sample substrates showed a good match with SCV for samples with ethane values less than -44‰. A closer evaluation also shows four main populations, samples with ethane values less than -60‰, perhaps from the secondary biogenic origin. Ethane values between -60‰ and -44‰ can be related to shallow coal bed sources (Tilley and Muehlenbachs, 2011) and those between -44‰ and -28‰ mature thermogenic origin, and samples heavier than -28‰ to deep, overmature thermogenic gases (e.g. Tilley and Muehlenbachs, 2011).

Propane and butanes in domestic water wells (WW) indicate unwanted thermogenic gas in problematic wells (Tilley and Muehlenbachs, 2011). Propane isotopic values were measured in 56 WW, 55 GM, and 360 SCV samples in the zoomed area (Fig. 26, and Fig. 27ac). These values describe a bimodal distribution, which overlaps among the sample substrates (Fig. 27ac). Samples can be divided into two main populations, those with values less than -35‰, and samples with enriched carbon isotopic values. Depleted carbon isotope values of -57‰ and -44‰ were observed in WW. Such values have been reported in studies conducted in the same area (Humez *et al*., 2019), and overlap with GM and SCV. Propane samples ranging between -35‰ and -28‰ may indicate that the WW, GM, and SCV gases come from the same source. *Iso*-butane and *n*-butane carbon isotopic distribution clearly show the overlapping distribution for all evaluated WW, GM and SCV. A common, mature, thermogenic origin would be proposed for these gases.

Carbon dioxide isotopic composition distribution for the evaluated samples shows a broad unimodal distribution. For WW and GM such values hover between -55‰ and -5‰, with very depleted values <-55‰. The carbon isotopic values describe methane oxidation, fermentation, and plant sources. Much more enriched carbon dioxide values correspond to production targets.

WW, GM, SCV and Production gases n-alkanes and carbon dioxide isotopic composition

A more detailed discussion of the geochemical data follows. We look again at the histograms and link them to crossplots of the isotopic composition of various components that make up the gas. Figure 28 shows a pairplot of WW, GM, SCV and production combing histogram of methane (Fig. 28 ai), ethane (Fig. 28 aii), and carbon dioxide (Fig. 28 aiii), above cross plots of methane vs. ethane (Fig. 28 aa), methane vs. CO2 (Fig. 28 ab), and ethane vs. carbon dioxide (Fig. 28 ac). Methane vs. ethane display a clear linear correlation and overlap among WW, GM, SCV and production oil-associated gases. Such correlation indicates a common source and unwanted fugitive free gas in these WW (Fig 28ab). A clear threshold can be observed. Those WW that show methane values less than-75‰ do not have other hydrocarbon gases (Fig 28aa, ab).

The plot of methane vs. CO_2 reveals a variety of processes: methane oxidation, methyl fermentation characteristic of freshwater, as well as carbon dioxide reduction (Whiticar, 1999; Humez *et al*., 2016a,b; Humez *et al*., 2019) (Fig. 28ab). Clearly, very enriched methane, ethane, and carbon dioxide carbon isotopic values show and share a common deep thermogenic source. The histogram distribution for ethane (Fig. 28bi), propane (Fig. 28bii), *iso*-butane (Fig. 28biii) and *n*-butane (Fig. 28biv), and their crossplots (Fig. 28ba-f), and thus the occurrence of propane and butanes in WW can be linked to energy wells and the fugitive gas migration to the ground (soils) as well as emissions through SCV. In this particular zoomed area, propane and butanes may be coming from production targets (Fig. 28b, d, e and f). These inferences and conclusions can be further tested statistically.

Statistical comparisons of the data discussed above were made using a simple kernel model. WW-Production gas–Fig. 29a; WW-SCV–Fig. 29b; and WW-GM–Fig. 29c depicts distribution normalized overlaps among samples in the zoomed area. Such results and their interpretation can be analyzed carefully and provide evidence about the source, mixing and potential reaction processes. Here, we plotted the carbon isotopic composition of *n*-alkanes and carbon dioxide in WW against production oil-associated gases, GM, and SCV.

The regional methane, ethane and carbon dioxide isotope values and correlations among domestic water wells, ground migration, SCV and production gases we report are per previous local studies in the same area that included a comprehensive set of hydrochemical parameters were such as: Eh/pH, salinity, total dissolved inorganics, and organics (e.g. Ryan *et al*., 2015). Notably, low ^{13}C ethane and propane have been reported (Humez *et al*., 2016a, b; Humez *et al*., 2019). Our observations agree with the previously identified geochemical processes in the area, which are characteristic of shallow and deep aquifers contained in coal bed seams common in the zoomed area. This study concentrates on answering the question related to the thermogenic origin of gases impacting domestic water wells in central Alberta, as was suggested by Tilley and Muehlenbachs (2012).

Thermogenic sourced gases, such as propane and butanes measured in production gases from the zoomed area, show a high statistical correlation with those analyzed in domestic water wells (Fig. 29aj, ak, am). Such correlation displays high tortoises and overlap of propanes, and butanes of the normalized kernel distribution for WW and production gas-associated gases (Fig. 29aiii; Fig. 29aiv, Fig29av). In this area, a similar response was observed for ethane, propane and butane isotope ratios paired WW with SCV (Fig. 29biii; Fig. 29biv, Fig29bv), and WW and GM (Fig. 29ciii; Fig. 29civ, Fig29cv) samples, which confirms that the isotopic values of ethane, propane and butanes are quite similar among samples collected in the area. However, there are only a few problematic wells that have propane and butanes. The isotopic composition of propane and butanes may identify the source of thermogenic gas in the domestic water wells but not methane. Thus, comparison among nearby sampling substrates (e.g. WW, GM and SCV) close to problematic domestic water wells might indicate the source, fate and distribution of such gases in the environment and their correlation with topography.

Relationship between topography and profiles

Methane, ethane and carbon dioxide isotope contour maps were generated for a zoomed area (Range 11 W4 to Range 6 W5, and Townships (T) from 20 to 53) and overlaid on topography (Fig. 30–35). Individual color-coded points were plotted for propane and butanes on Fig. 36a, b, which were detected in only a few locations. Inspection of the contour map for methane (Figs. 30 & 31) and of ethane Figs. 32 & 33 shows distinct geographic patterns, “hot spots” on a scale of kilometers within which multiple domestic water wells have relatively similar enriched isotopic values (warm colors), suggesting localized impacts of relatively large plumes of thermogenic gas.

To examine in detail the potential impact of leaking energy wells on domestic water wells, we constructed cross-sections and profiles as laid out in Fig. 37, linking topography and the isotopic compositions. Some of the profiles were chosen to cross the “hot spots” and link as many of the wells as possible. All profiles show the topography (meters above sea level) but the isotopic profiles in Figs. 38 to 41 connect only domestic water wells. Other profiles include both water wells and surface casing (Figs. 42–43), and water wells, surface casing and additionally, ground migration (Fig. 44–45). It should be noted that each profile is of differing length but plotted on the page’s width. Note also that the isotopic scales are inverted.

Profile A - A’ (Fig. 38) is 80 km long in the southwest of the zoomed region that has many water wells and crosses one such “hot spot” (see Fig. 30 & 32) where the methane values go from the regional average of -65‰ to -40‰ at 40,000 m on the profile. The ethane values do not show a dramatic matching change at 40,000 m, but along most of the profile, the ethane values are richer in ^{13}C than the general background values. One can argue that A - A’ crosses a plume of admixing thermogenic gas.

Profile B - B’ (Fig. 39) is shorter, 18 km, parallel and northwest of A - A’ but crosses the highest density of water wells on the NW edge of the “hot spot”. Methane values do not vary dramatically as in A - A’, but do dip. Ethane values decline dramatically at 15,000 m to thermogenic values and match ethane values on A - A’. A simple suggestion is that methane and ethane's transport are decoupled in the putative plume of thermogenic gas.

Profile C - C’ (Fig. 40) is 120,000 m long, crossing the center of the study area. It starts on a “hot spot” for methane, crosses another one about 60,000 m visible only in the ethane values and ends at normal background water well. A simple suggestion is that in putative plumes of thermogenic gas, the transport and origin of methane and ethane are decoupled.

Profile E - E’ (Fig. 41) is in the north of the study area, is 60 km long but does not cross any “hot spots”. Interestingly the isotopic composition of CO_2 shows extreme depletion at about 25,000 m matched by a slight enrichment in methane that is indicative of localized hydrocarbon oxidation within the aquifer at a topographic low or valley.

Profile G - G’ (Figs. 42a, b. c, d) is 70,000 m long and south of E -E’. This profile includes energy wells with SCV in addition to the domestic water wells. In the water wells, the methane, ethane and CO_2 values are correlated and vary significantly along with the profile, from relatively negative in the west to more positive in the east. Figs. 42b, 42c and 42d show that isotopic variations of methane, ethane and CO_2 along SCV along this profile mimic those of the domestic water wells suggesting that such gas escaping from energy wells may be impacting the aquifer there.

Profile H - H’ (Fig. 43a, 43b and 43c) includes both water wells and SCV, is 180,000 m long and crosses a “hot spot” at about 90,000 m. The methane values in domestic water wells there increase from -68‰ to -50‰, reaching thermogenic values, but CO_2 values remain at background levels. In contrast, the ethane values are sporadic and more variable than seen in the other profiles (Fig. 43a). The SCV methane values are quite uniform along with the profile but match the water well methane values at the 90,000 m mark.

Fig. 43c compares ethane from water wells to the SCVs. Both are variable along with the profile but do not covary or overlap. No explanation of the isotopic variations is obvious along H - H' except that methane and ethane's transport and origin are decoupled.

Profile F - F' crosses the study area diagonally from SE to NW is 280,000 m long and includes water wells, SCV and GM. F - F' avoids obvious "hot spots'' except for ethane at about 120,000 m. Overall, along with the profile, the isotopic composition of water well methane and ethane varies in parallel within the average background range. An important observation should be made that the background water methane values follow topography most visible in F - F' and I - I', but could be inferred from the other profiles. Such a relationship gives an insight into how methane is being generated within an aquifer as it flows due to gravity drive. A Rayleigh type isotope fractionation may be controlling the isotopic composition of the evolved methane. F - F' profile also includes GM and SCV (Fig. 44b, 44c and 44d). Of note is that the dip in water ethane value at 120,000 m to -40‰, which matched by ethane in GM, but SCV methane is much richer in ^{13}C.

Profile I - I' goes south on the western edge of the study area and is 200,000 m long. No "hot spots" were crossed. The methane and ethane isotopic compositions are subparallel and well correlated with topography (Fig. 45a). As with F - F', I - I' also includes GM and SCVF, whose methane values are not correlated with the water wells (Fig. 45b). The ethane values of GM and SCV are correlated (Fig. 45c), indicating unsurprisingly that the GM accompanies SCV flow along with this profile. Unexpectedly, the water well CO_2 profile (Fig. 45a) shows extreme oxidation of hydrocarbons in the aquifer at the beginning of the profile at a topographic low and least oxidation at the adjoining topographic high in contrast to what is seen with CO_2 in GM where minimum oxidation is at low topography. Still, maximum oxidation is at about 120,000 m at higher elevations (Fig. 45d).

Comparison of contour maps of methane and ethane for WW, GM and SCV

Figures 46 and 47 complemented Figures 30 to 35 by directly comparing the isotope contour maps of WW, GM and SCV, respectively, in our zoomed area. Please note that the color scale for each map is different. Observations in this report underline the necessity of conducting more comprehensive hydrological and geological studies in the "hot spot" areas identified on our isotope contour maps and profiles. Areas where multiple domestic water wells may be regionally impacted by thermogenic gas. Fundamental hydrogeological, geological and engineering knowledge will be required to depict the mechanisms controlling thermogenic gas plumes and input in domestic water wells and soils in this area.

F. KEY LEARNINGS

Hydrocarbon gases are frequently found in domestic water wells of Alberta. We found that in about 90% of the cases, the methane in domestic water wells had a very low content of ^{13}C indicative of being derived from microbes within the aquifer. Local microbial origin within a flowing aquifer is evidenced by the observation that the assumed biogenic methane isotope values follow topography reflecting the water's flow path. However, some domestic water wells have free thermogenic butanes, propane and ethane, which can not be formed by microbes. Their isotopic composition proves that the propane and butanes are deep and thermogenic. Propane and butanes isotopic composition from domestic water wells matches the isotope values of propane and butane from nearby energy wells indicating faulty energy wells may be the source of thermogenic gas in domestic water wells. Many of the impacted water wells are geographically grouped, suggesting a regional impact of deeper thermogenic gas on given aquifers allowing for the possibility that localized geological faults may have provided pathways for deep thermogenic gas to enter shallow aquifers. Our mapping of isotope values of hydrocarbon gases in domestic water wells has identified specific regions where water wells are more likely to be impacted by thermogenic gas. Those regions also have many energy wells. Resolving the ultimate source of thermogenic gas in domestic water wells requires detailed hydrogeological, geophysical and geochemical studies coupled with “forensic” assessments of the integrity of all the energy wells within the region.

G. OUTCOMES AND IMPACTS

This project provides maps and profiles showing the stable carbon isotopic variation of hydrocarbon gases in selected sampled Alberta's domestic water wells, as well as complimentary maps and profiles of fugitive hydrocarbon gases from energy wells. The data show that in most cases, the flammable gas is shallow, local and bacterially derived. However, certain regions have multiple domestic water wells that show the impact of deeper thermogenic gases comparable with the isotope fingerprint of ground migration, surface casing vent flow and production gas from nearby energy wells.

Regulators and industry should investigate why deep thermogenic gases impact multiple domestic water wells in select regions. For further detail, please refer to section recommendation and next steps.

H. BENEFITS

Economic: Our maps and profiles add considerable value to the raw isotopic data collected by industry mandated by the Baseline Water Well program for the CBM wells. Knowledge of geographically overlaying isotope fingerprints of domestic water wells, ground migration, surface casing, and production gases should lower any remediation projects' cost. In addition, our maps provide an isotopic baseline of hydrocarbons occurrence in water well in areas yet to be developed.

Environmental: We have identified specific regions in central Alberta where domestic water wells may be impacted by deeper thermogenic gases emanating from resource wells.

Social: Domestic consumers of groundwater in central Alberta should see that for the most part, any hydrocarbon gas from their water tap is of shallow and local origin. However, some consumers in the region should be warned of the potential impact of thermogenic gases on their water well.

Building Innovation Capacity: This project employed three people part-time, utilizing and improving their skills in data analyses and GIS methods. Graphic programs and databases are in place at the University of Alberta to generate as needed isotope contour maps at any scale and any region of choice.

I. RECOMMENDATIONS AND NEXT STEPS

The observation that the isotopic composition of methane in unimpacted domestic water wells follows topography needs to be investigated by standard models of gravity-driven hydrogeological flow. The inference that fugitive gases from energy wells have in select regions impacted multiple domestic water wells needs to be documented. Determining the depths and age of the water wells, the local geology, the drilling history of both the water wells and neighbouring energy wells may elucidate the mechanism of any impact. A decade has elapsed since most of the water wells were tested. Reanalyses of selected wells along some of our profiles may reveal the rate of spread of any plumes of deeper thermogenic gas. Such a secular sampling study would fit with the above suggested hydrogeological and hydrogeochemical field study.

J. KNOWLEDGE DISSEMINATION

This project will be presented at the forthcoming European Geochemical Union meeting in April 2021. A manuscript for publication in a scientific journal is in preparation. Also, this complete report will be available for public dissemination. Unsolicited copies of this report will be sent to appropriate persons at AER, AEP and Industry.

K. CONCLUSIONS

We have provided an overview of isotopic compositions of hydrocarbon gases exsolving from domestic water wells of Alberta. About 90% of the hydrocarbon gases in domestic water wells are shallow and locally derived by microbes. The carbon isotope ratio of these biogenic methanes does vary and follows topography suggesting in situ methane generation along a flowing aquifer. However, some domestic water wells have free thermogenic butanes, propane and ethanes indicating an impact of thermogenic gas on the aquifer. The isotope composition of propane and butane of such impacted domestic water wells matches those of nearby energy wells, indicating faulty energy wells as the ultimate source of thermogenic gas in domestic water wells. Many of the impacted water wells are geographically grouped, suggesting a regional impact of deeper thermogenic gas on selected aquifers. Our regional mapping of hydrocarbon gases in domestic water wells has identified specific regions needing detailed hydrogeological and geochemical investigation.

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Figure 47. Comparison of contour maps of ethane carbon isotopic composition from domestic water wells (WW), ground migration (GM) and surface casing vent (SCV) in zoomed area. To the right of each map the color-coded legend is related to the sourced gas; warm color represents enriched carbon gases, whereas cold colors represents depleted carbon isotopic values gases.

Fig. 1. Location map of sampled domestic water wells (WW) gases in this study

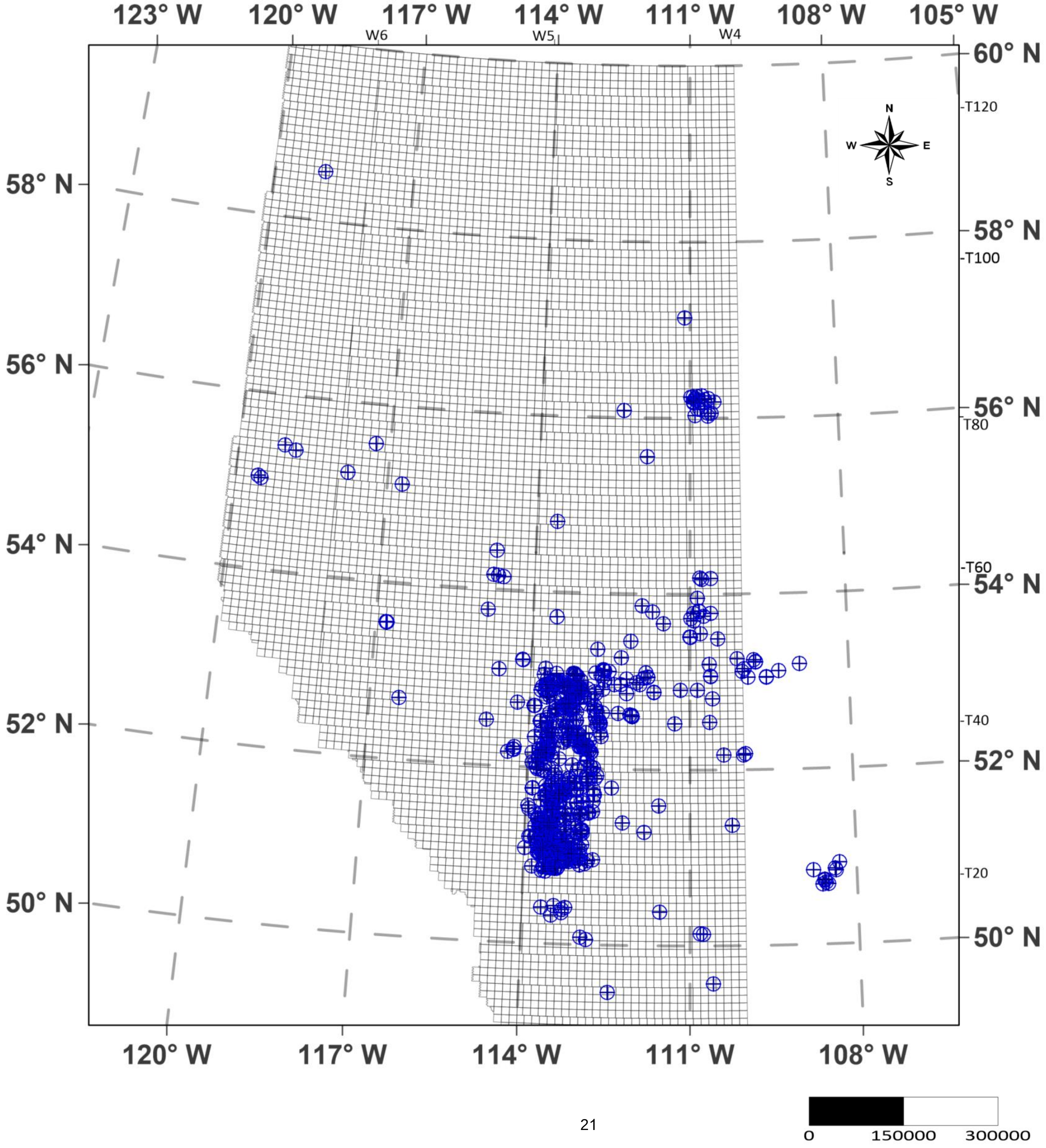


Fig. 2. Location map of sampled ground migration (GM) gases in this study

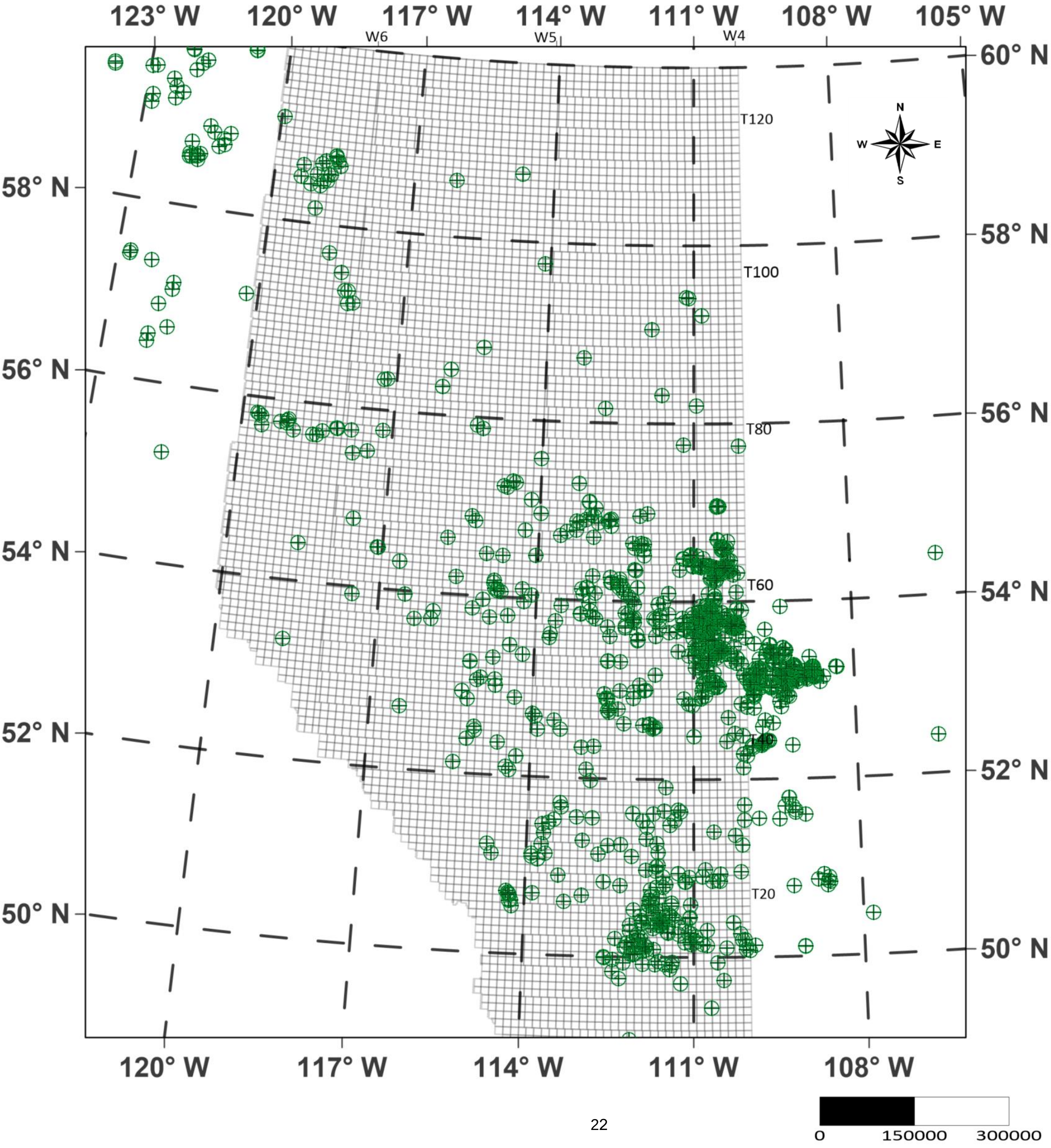


Fig. 3. Location map of sampled surface casing vent (SCV) gases in this study

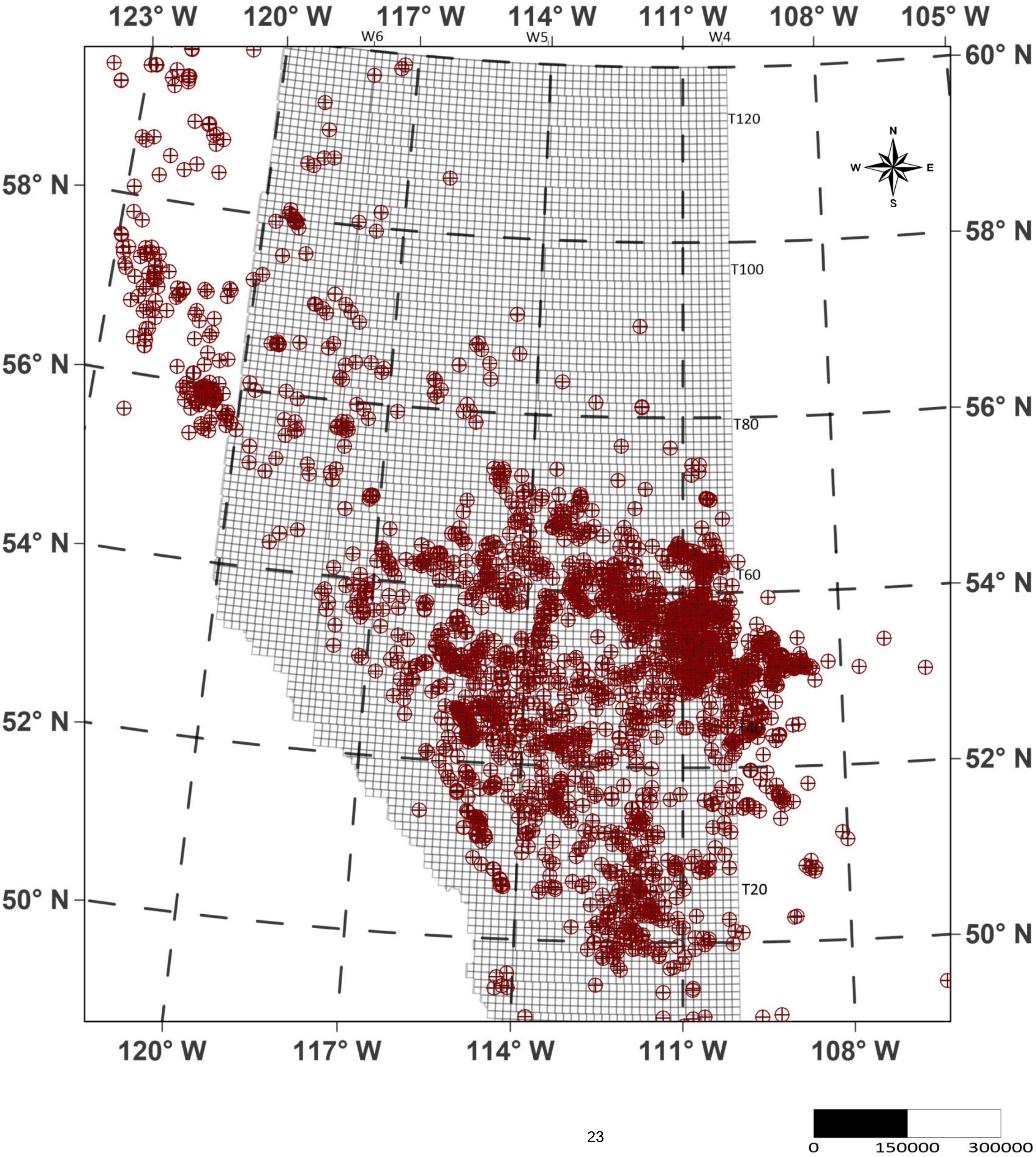


Fig. 4. Location map of sampled production oil-associated gases in this study

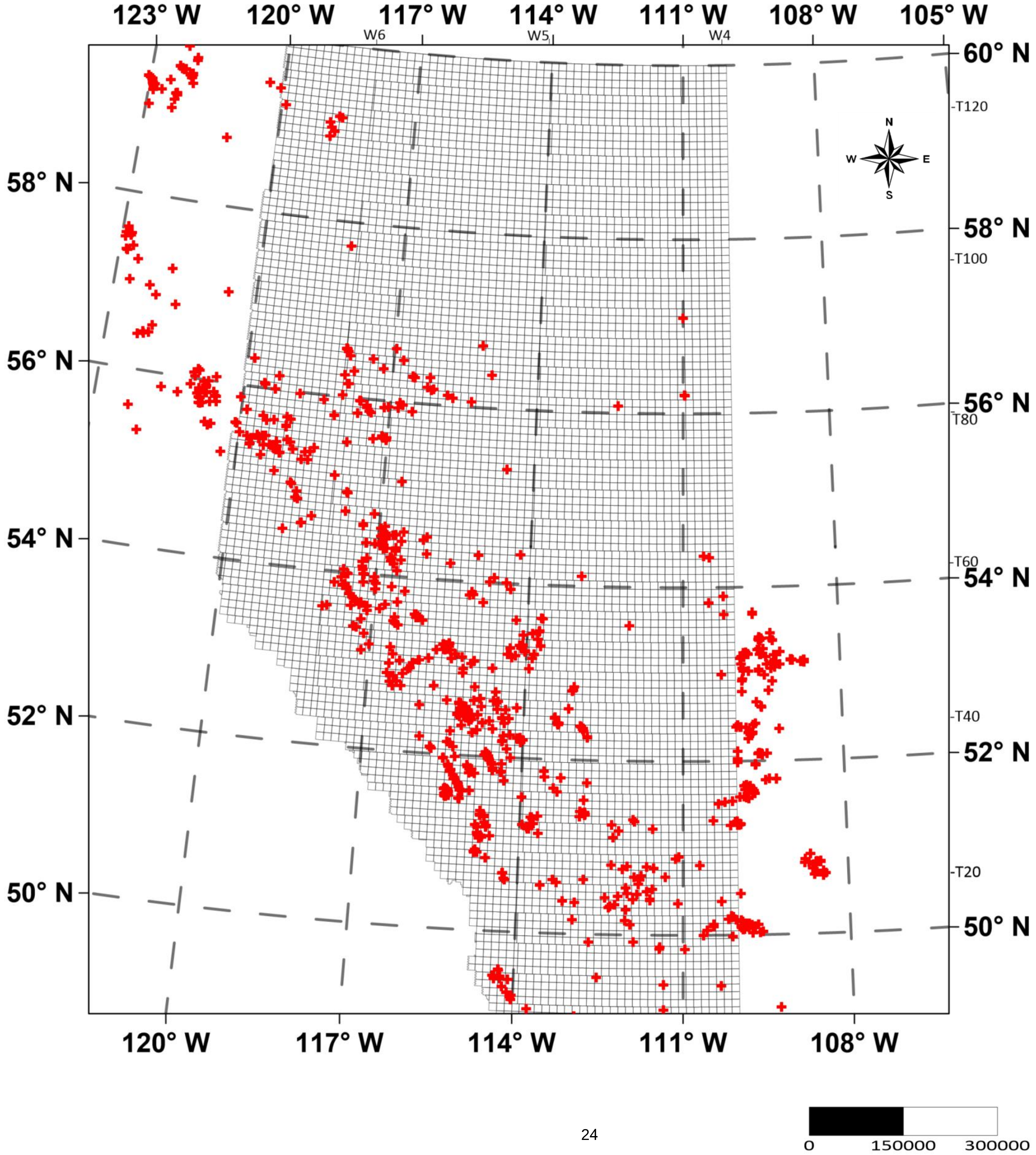
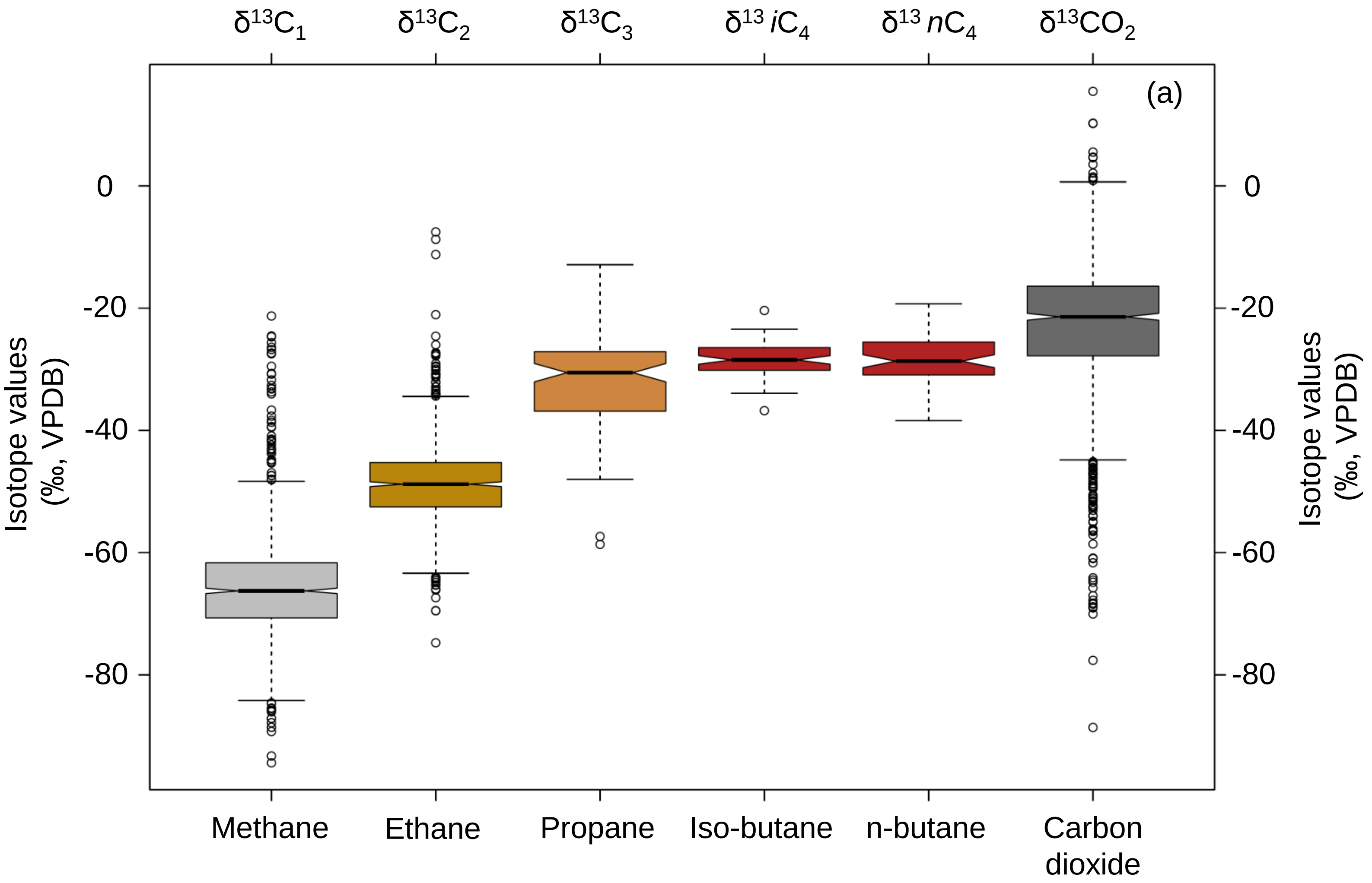
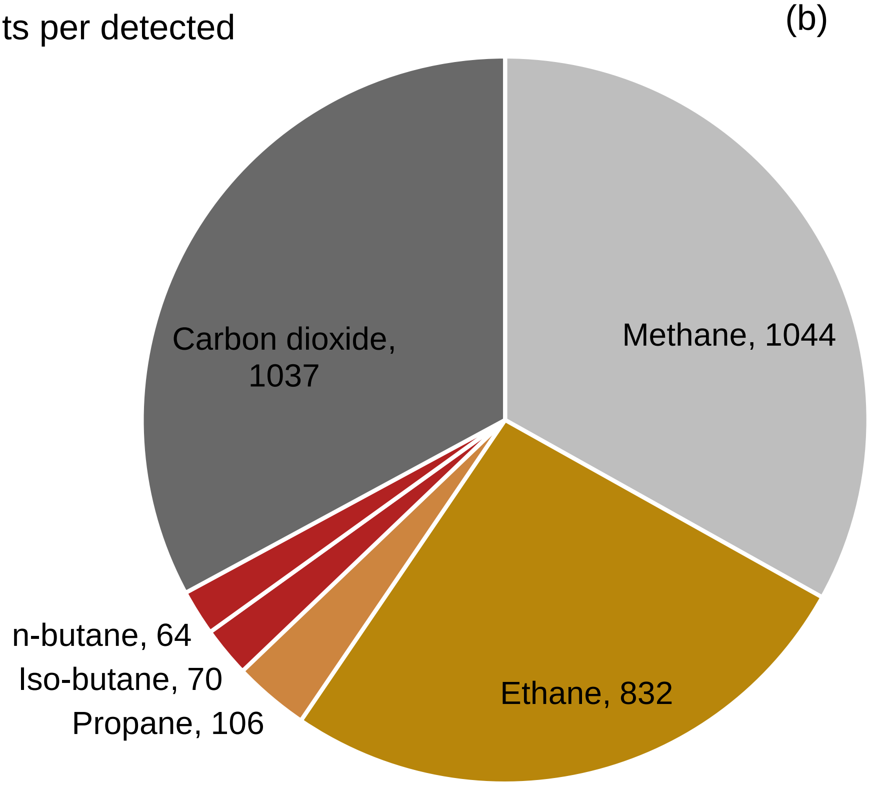


Fig. 5. Statistical analysis of methane, ethane, butanes and carbon dioxide carbon isotopic composition analyzed in sampled domestic water wells (WW)



Number of measurements per detected and analyzed variables

- ✓ The detection of butanes indicates thermogenic gas in water wells
- ✓ Thermogenic gas was detected in 6% of our sampling points
- ✓ In 65% of water wells tested, only carbon dioxide was detected and analyzed



Total number of samples: 1124

Fig. 6. Contour map of methane carbon isotope values of domestic water wells (WW)

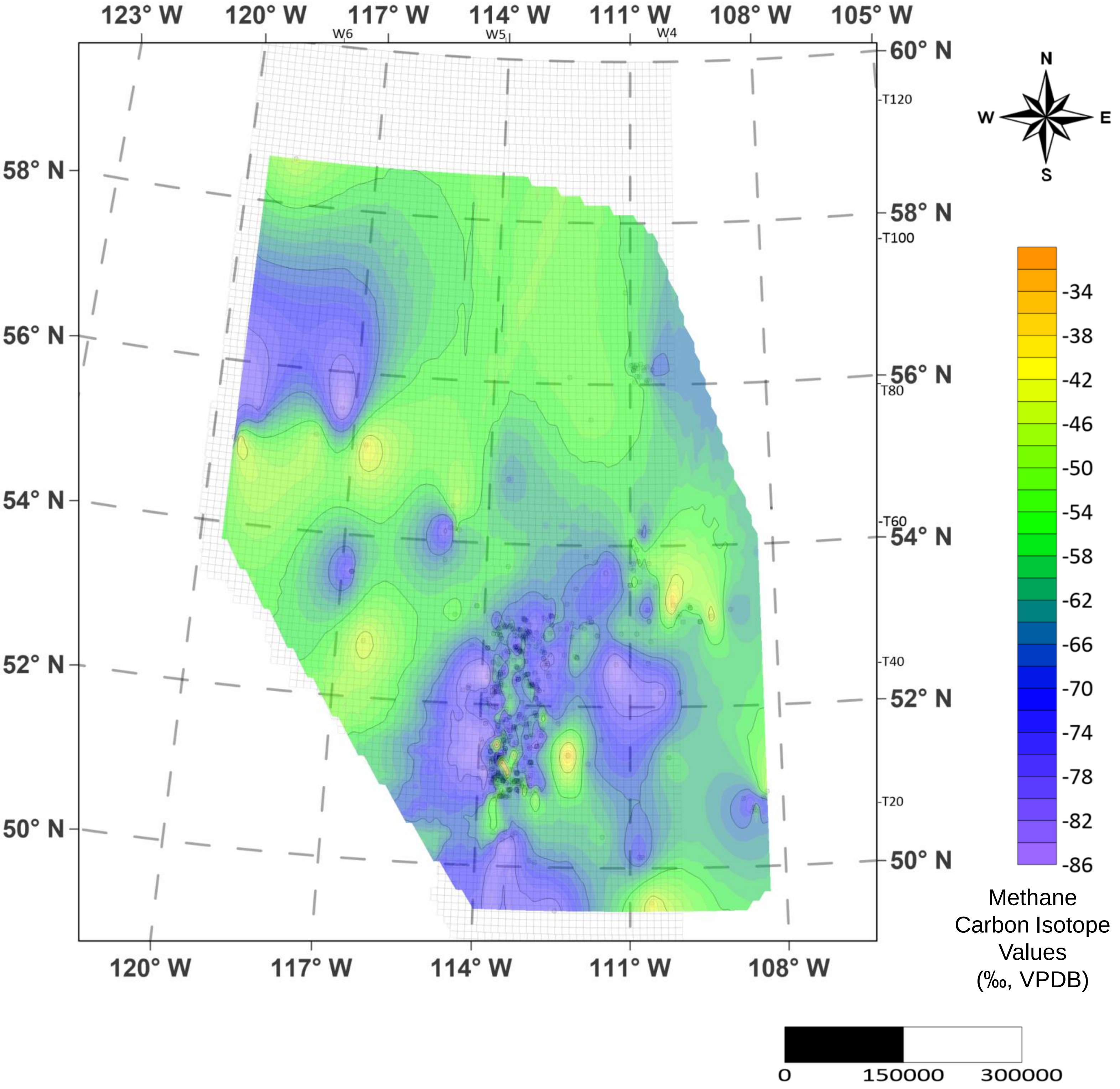


Fig. 7. Contour map of methane carbon isotope values of domestic water wells (WW) laid over topography

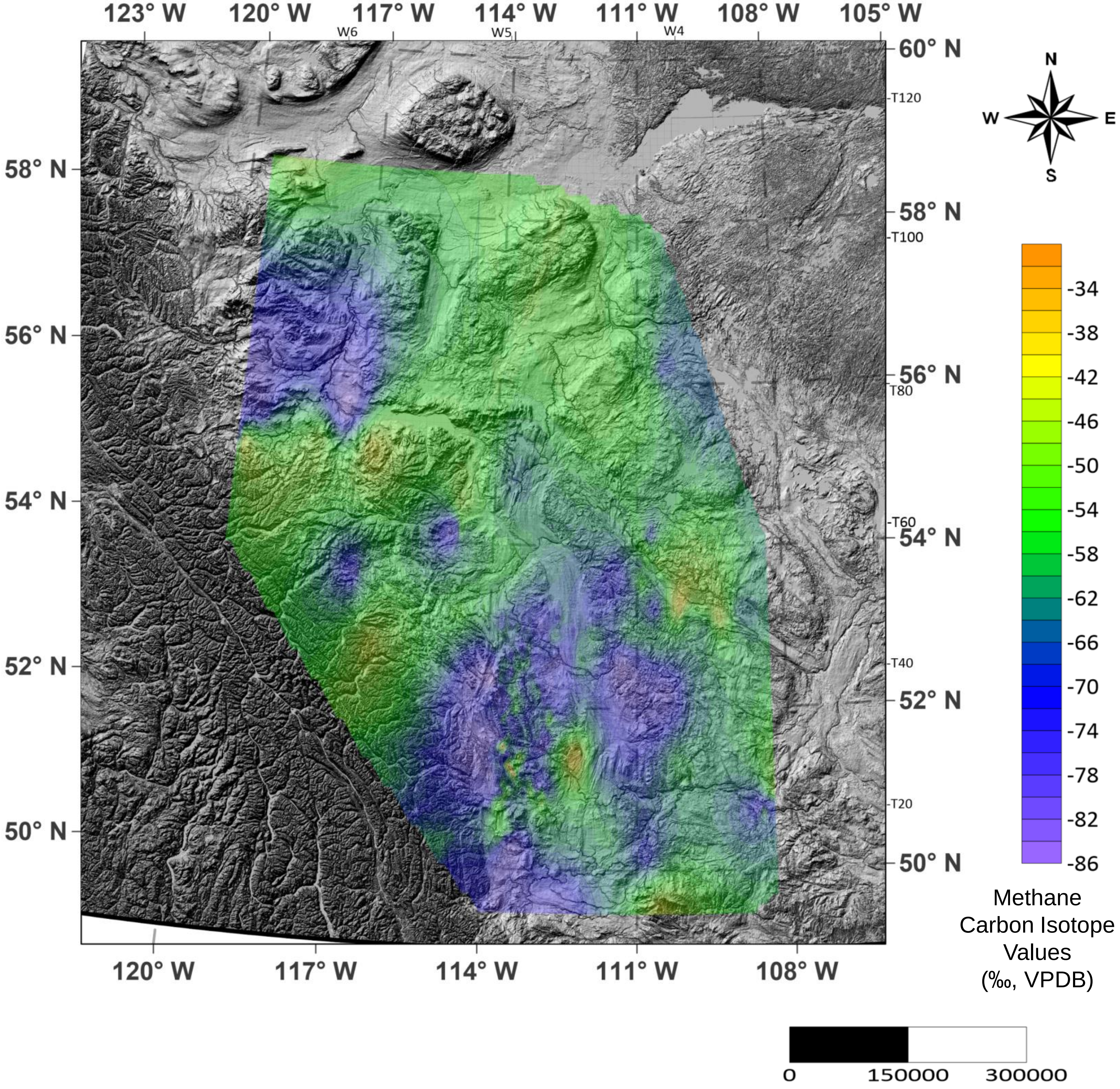


Fig. 8. Contour map of ethane carbon isotope values of domestic water wells (WW)

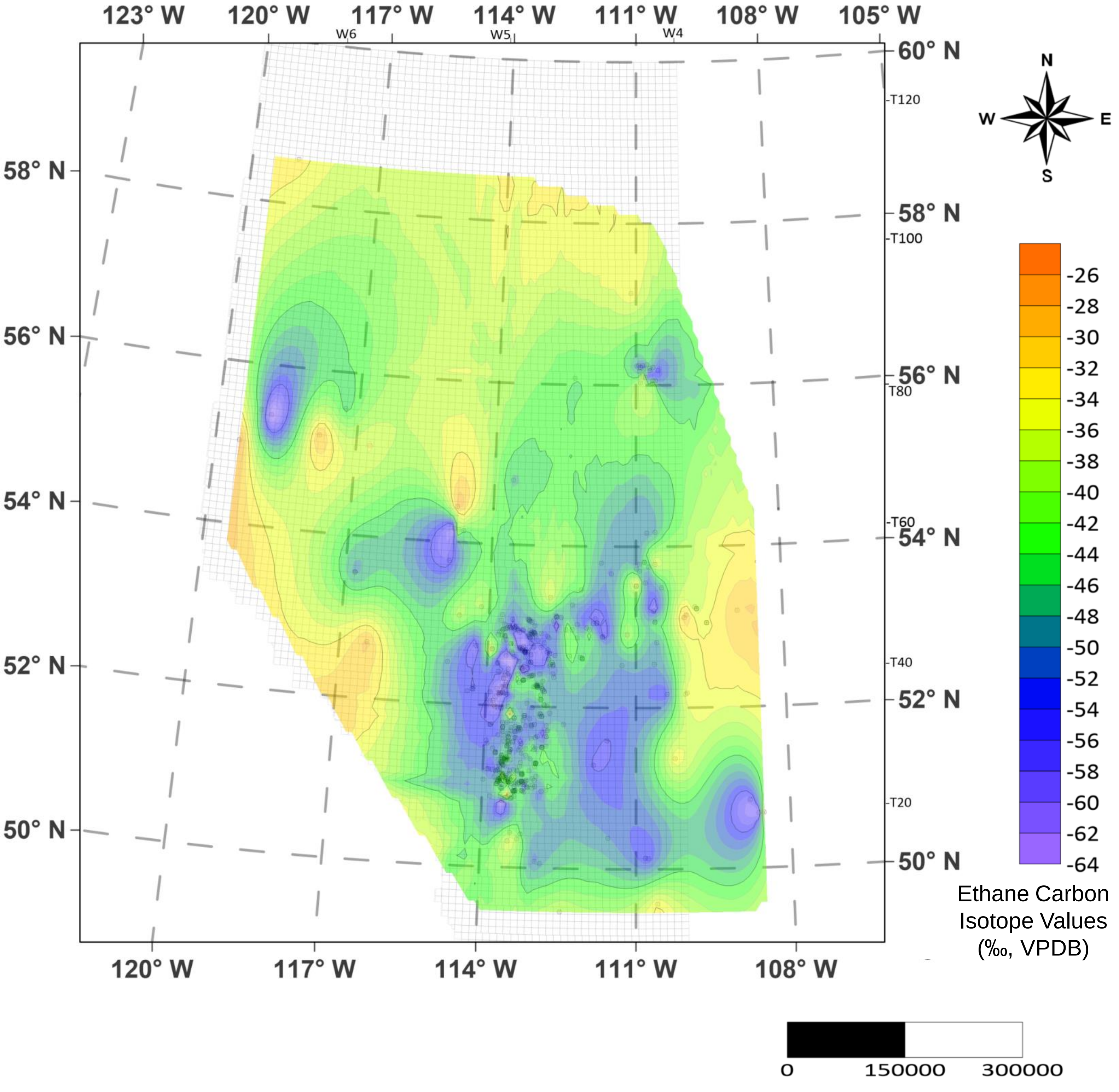


Fig. 9. Contour map of ethane carbon isotope values of domestic water wells (WW) laid over topography

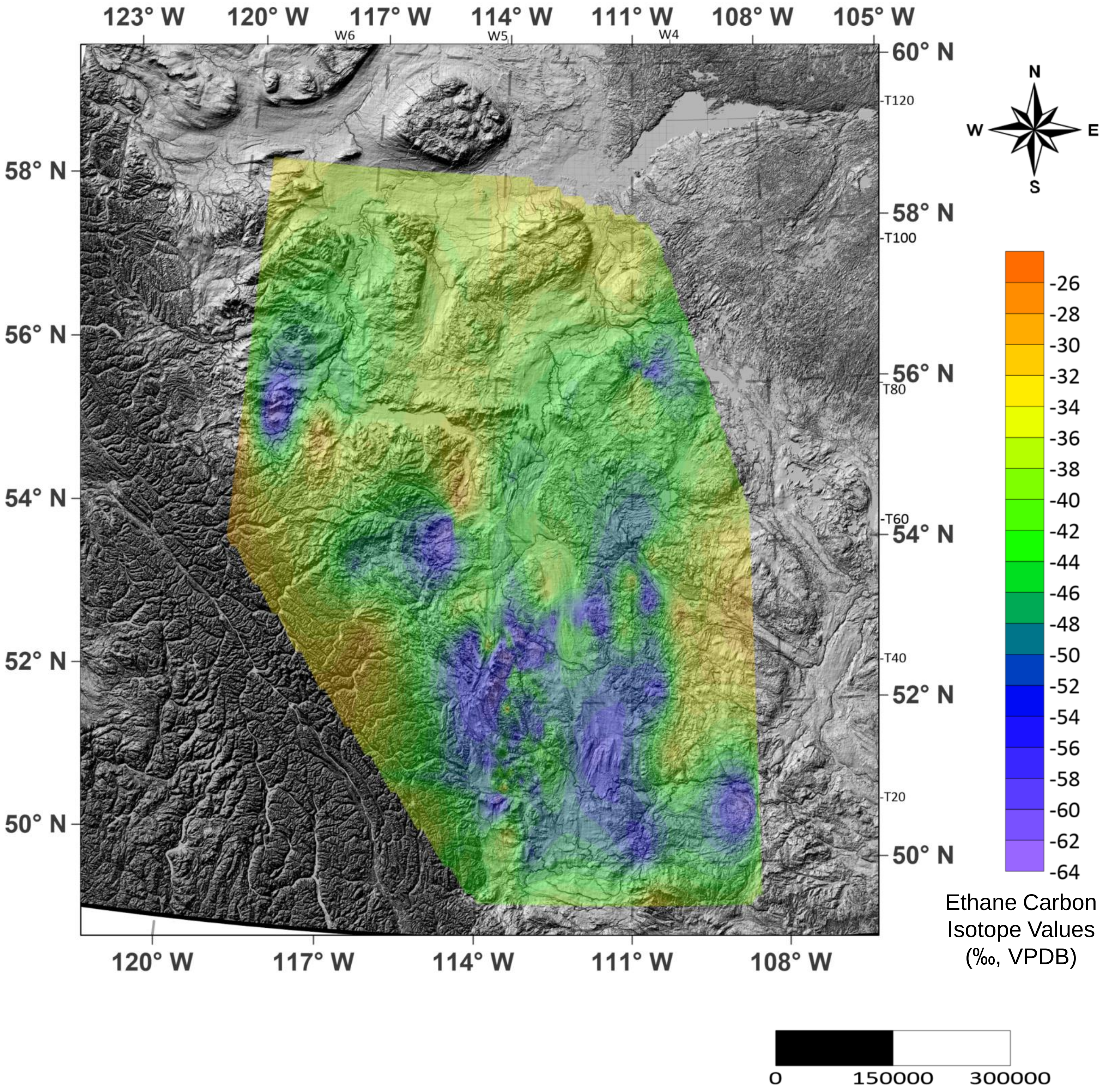


Fig. 10. Contour map of carbon dioxide carbon isotope values of domestic water wells (WW)

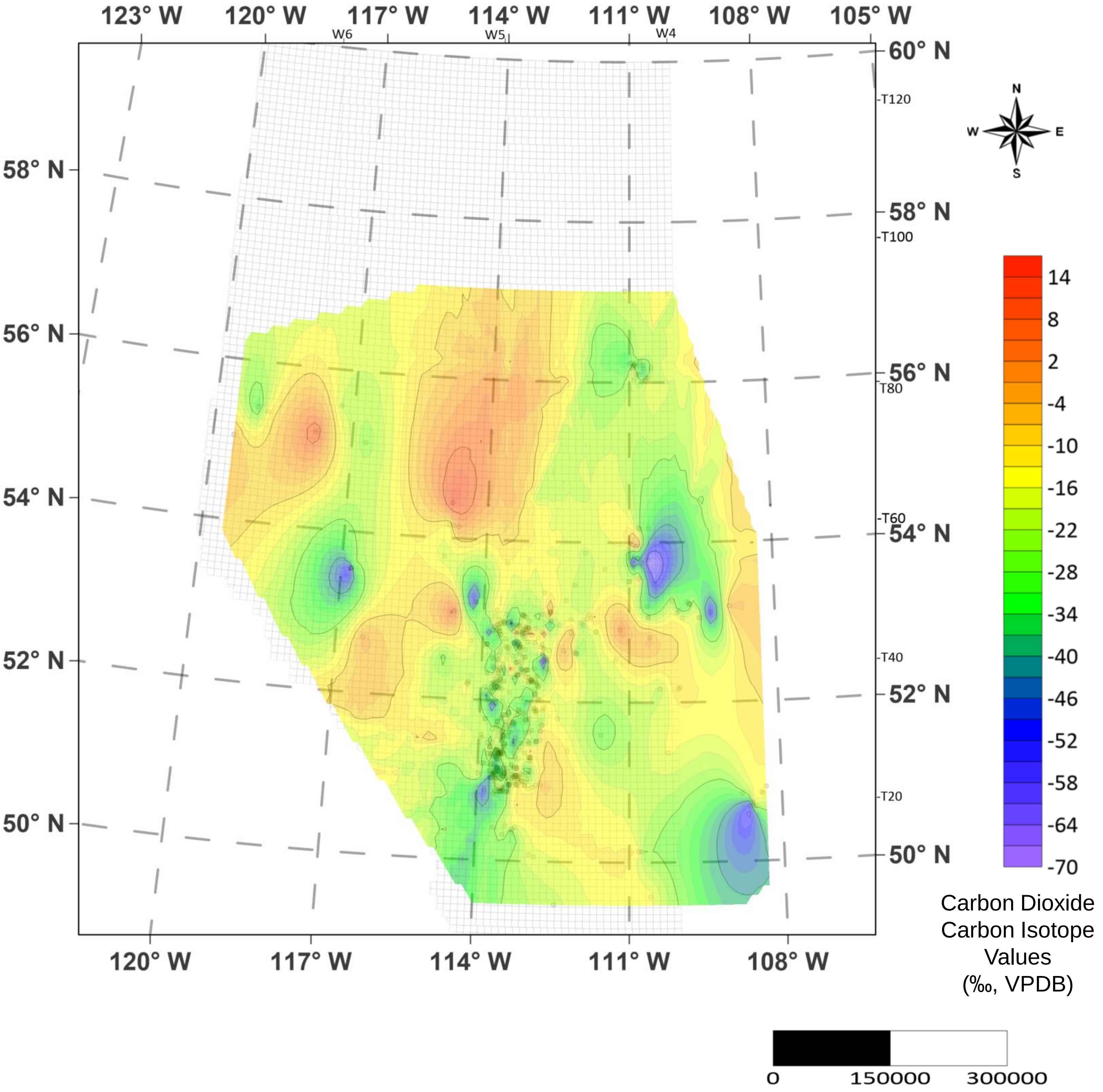


Fig. 11. Contour map of carbon dioxide carbon isotope values of domestic water wells (WW) laid over topography

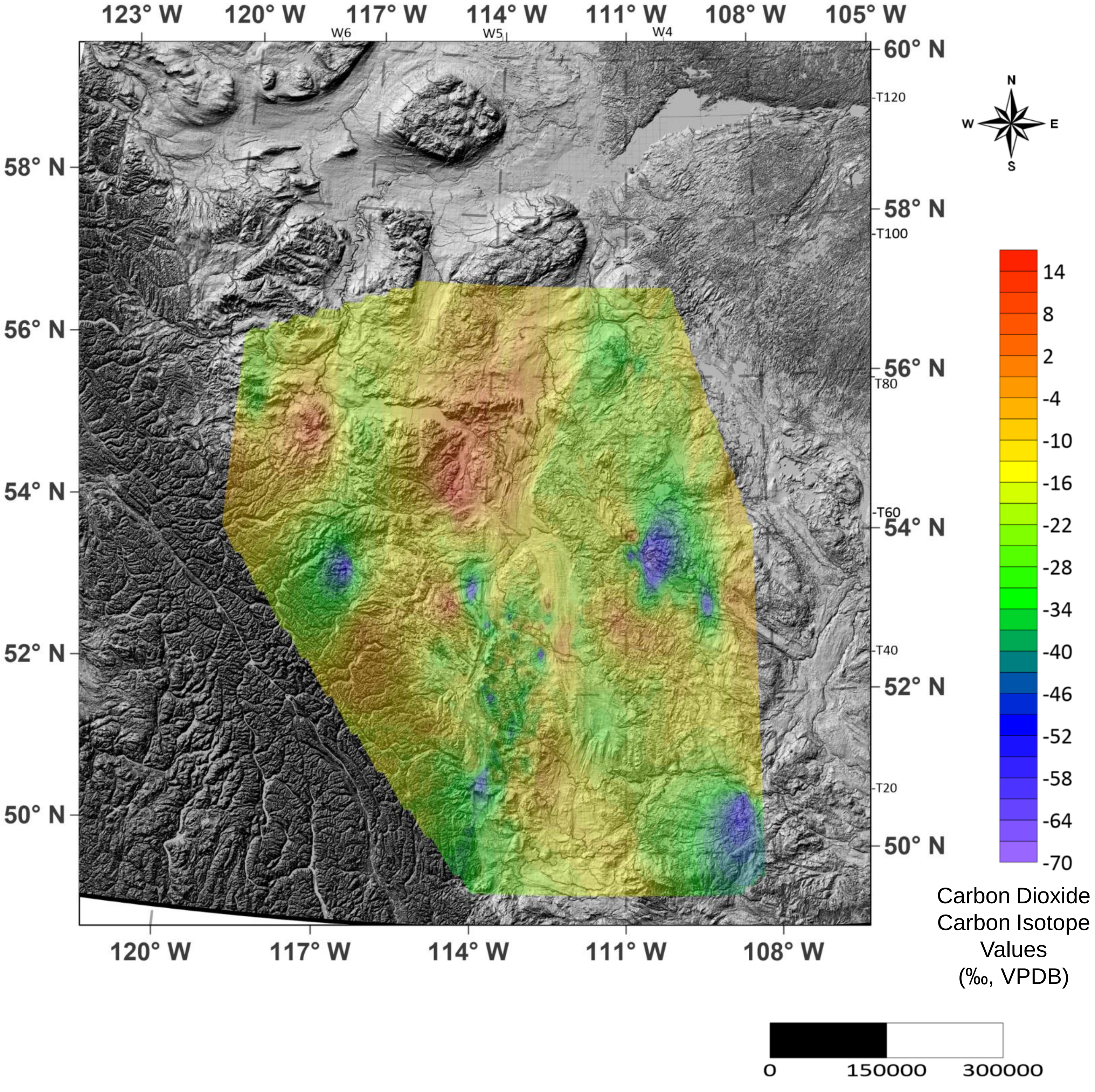


Fig. 12. Contour map of methane carbon isotope values of ground migration (GM)

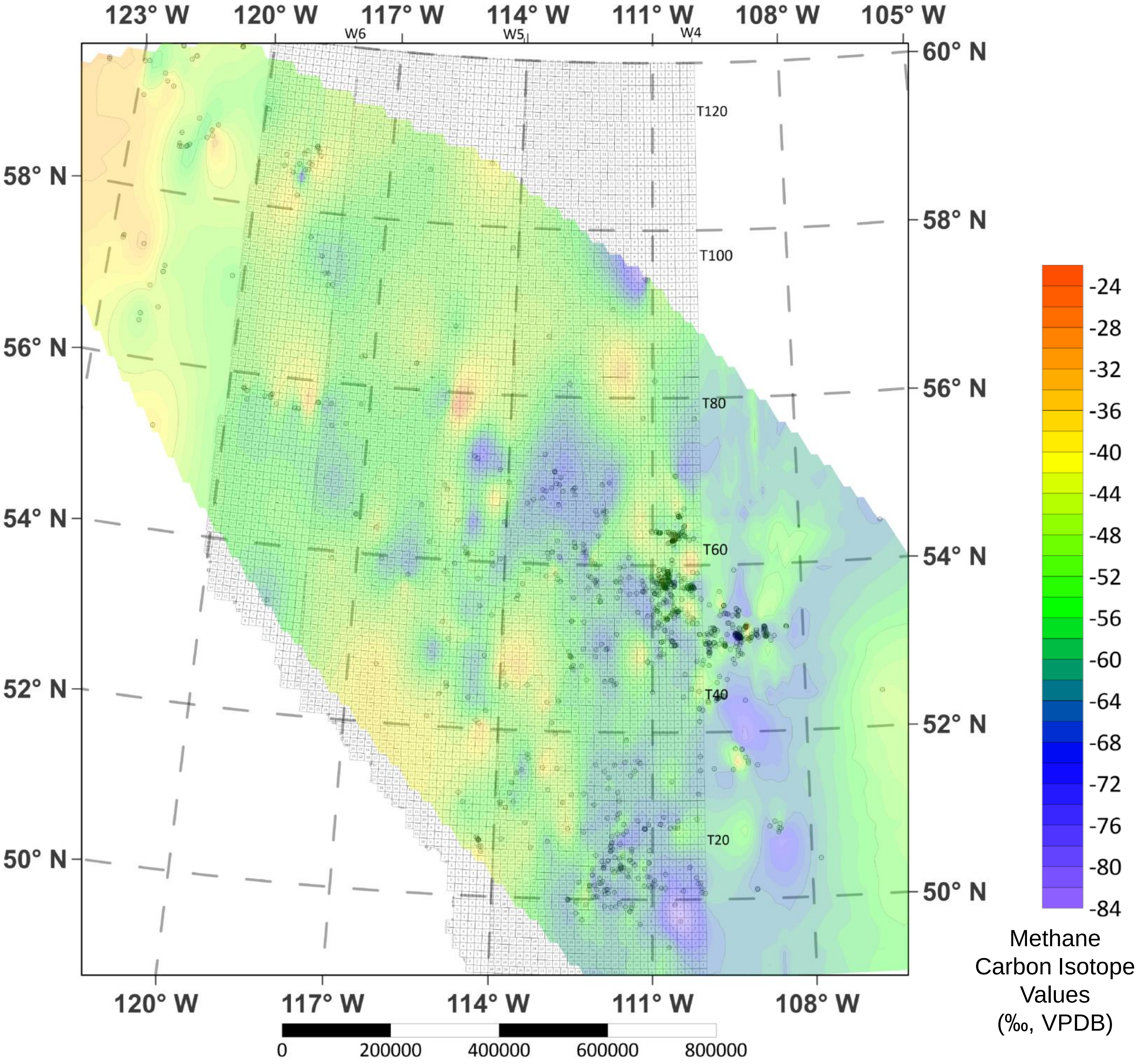


Fig. 13. Contour map of methane carbon isotope values of ground migration (GM) laid over topography

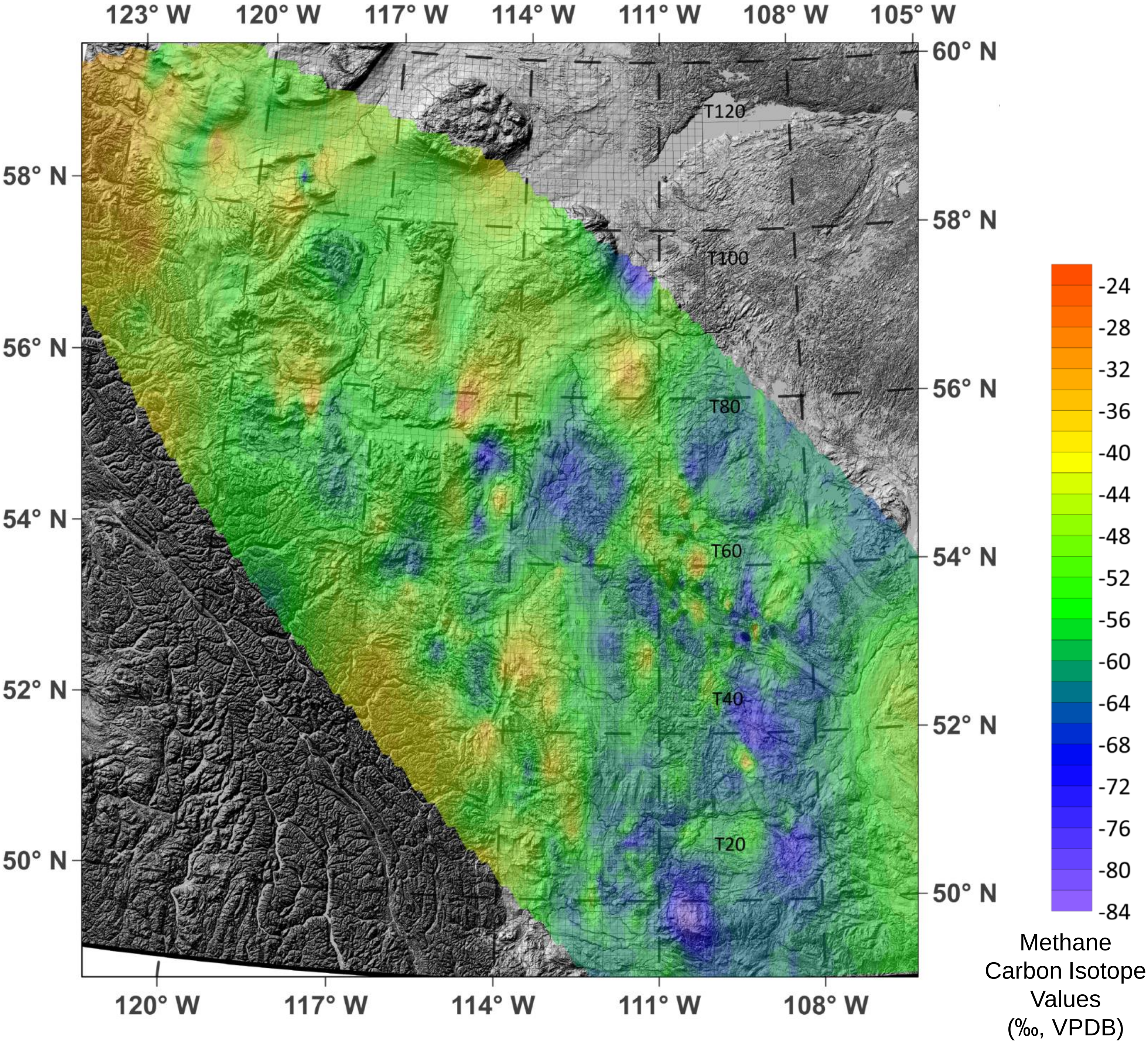


Fig. 14. Contour map of ethane carbon isotope values of ground migration (GM)

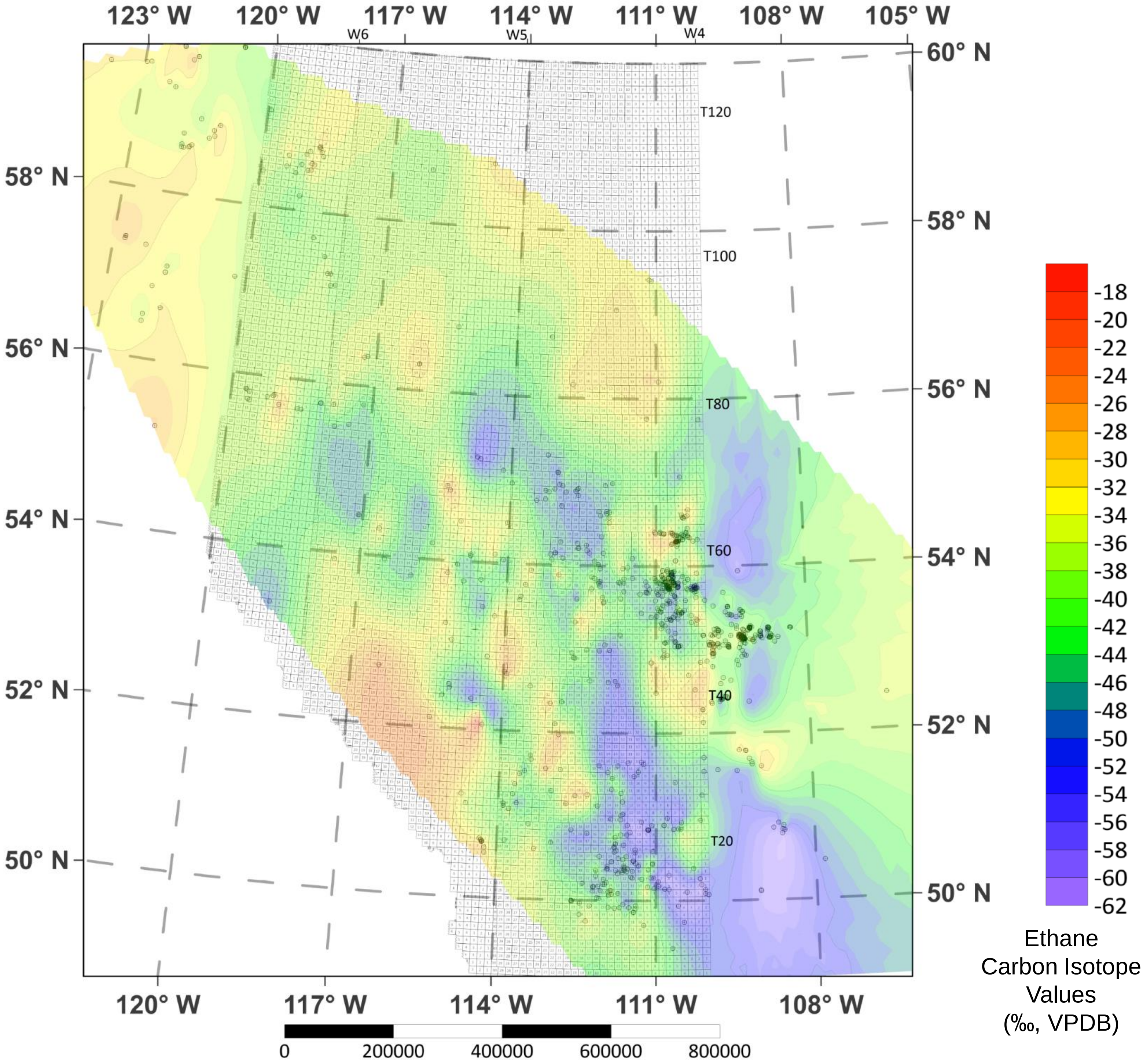


Fig. 15. Contour map of ethane carbon isotope values of ground migration (GM) laid over topography

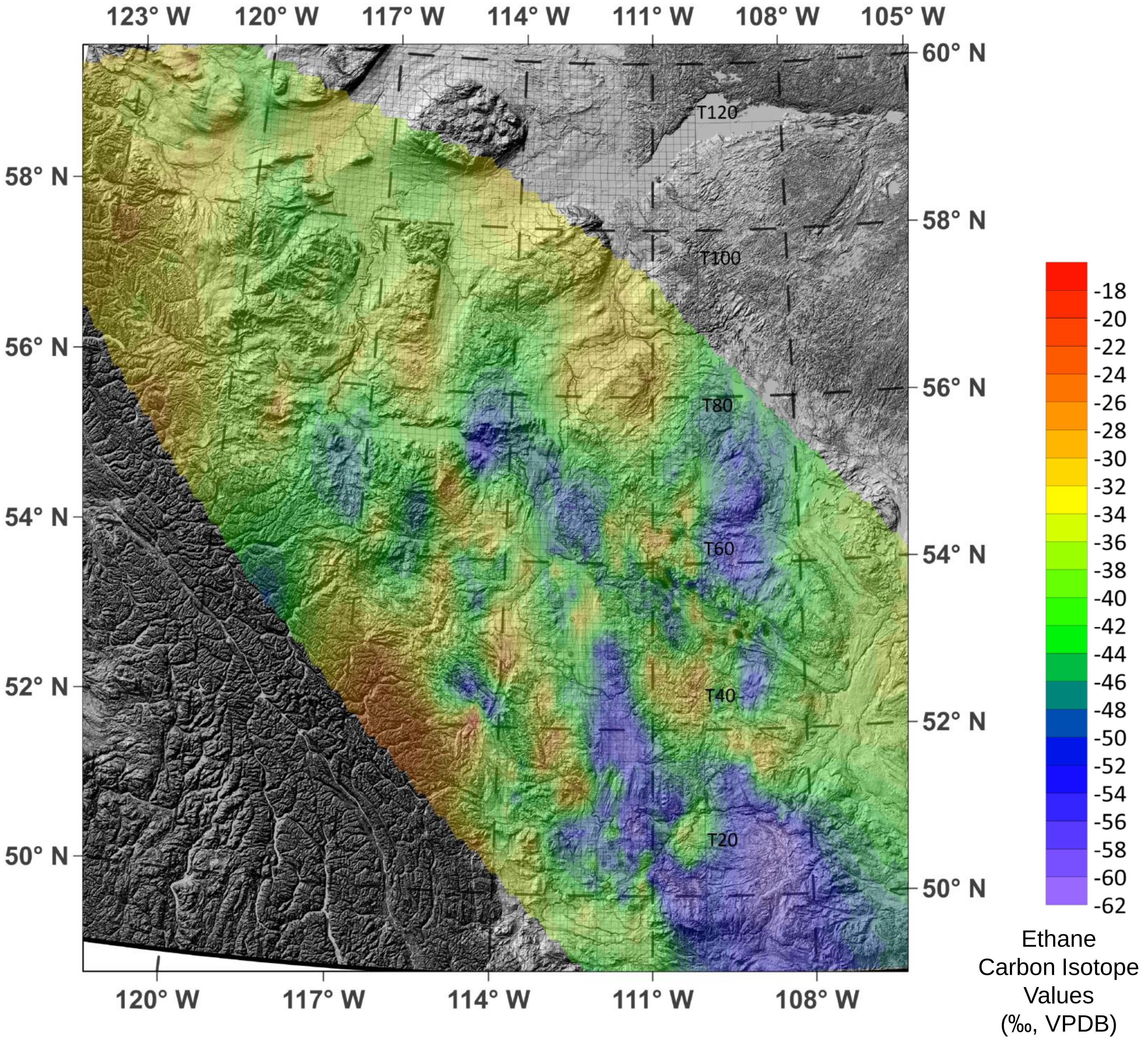


Fig. 16. Contour map of methane carbon isotope values of surface casing vent (SCV)

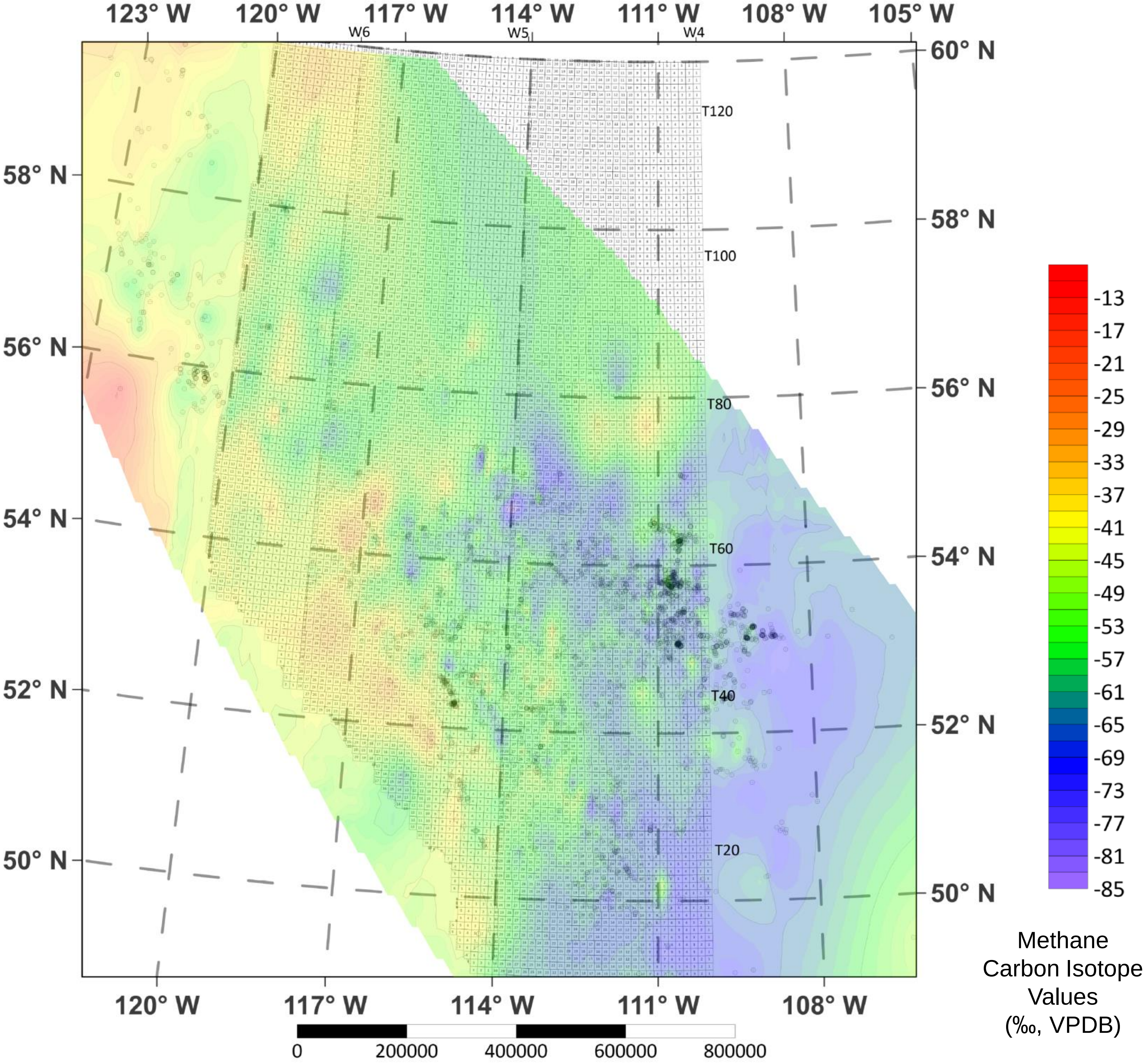


Fig. 17. Contour map of methane carbon isotope values of surface casing vent (SCV) laid over topography

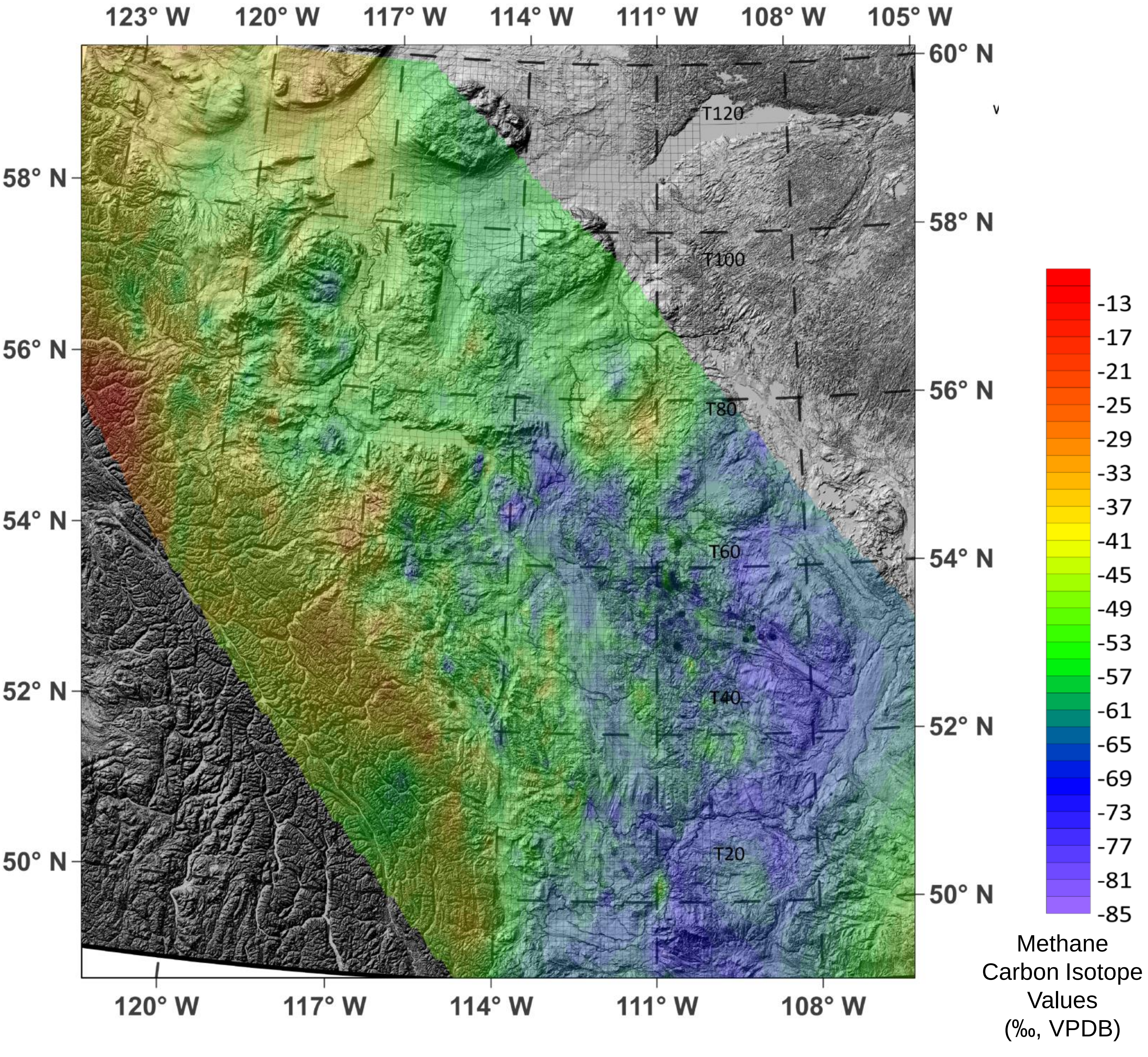


Fig. 18. Contour map of ethane carbon isotope values of surface casing vent (SCV)

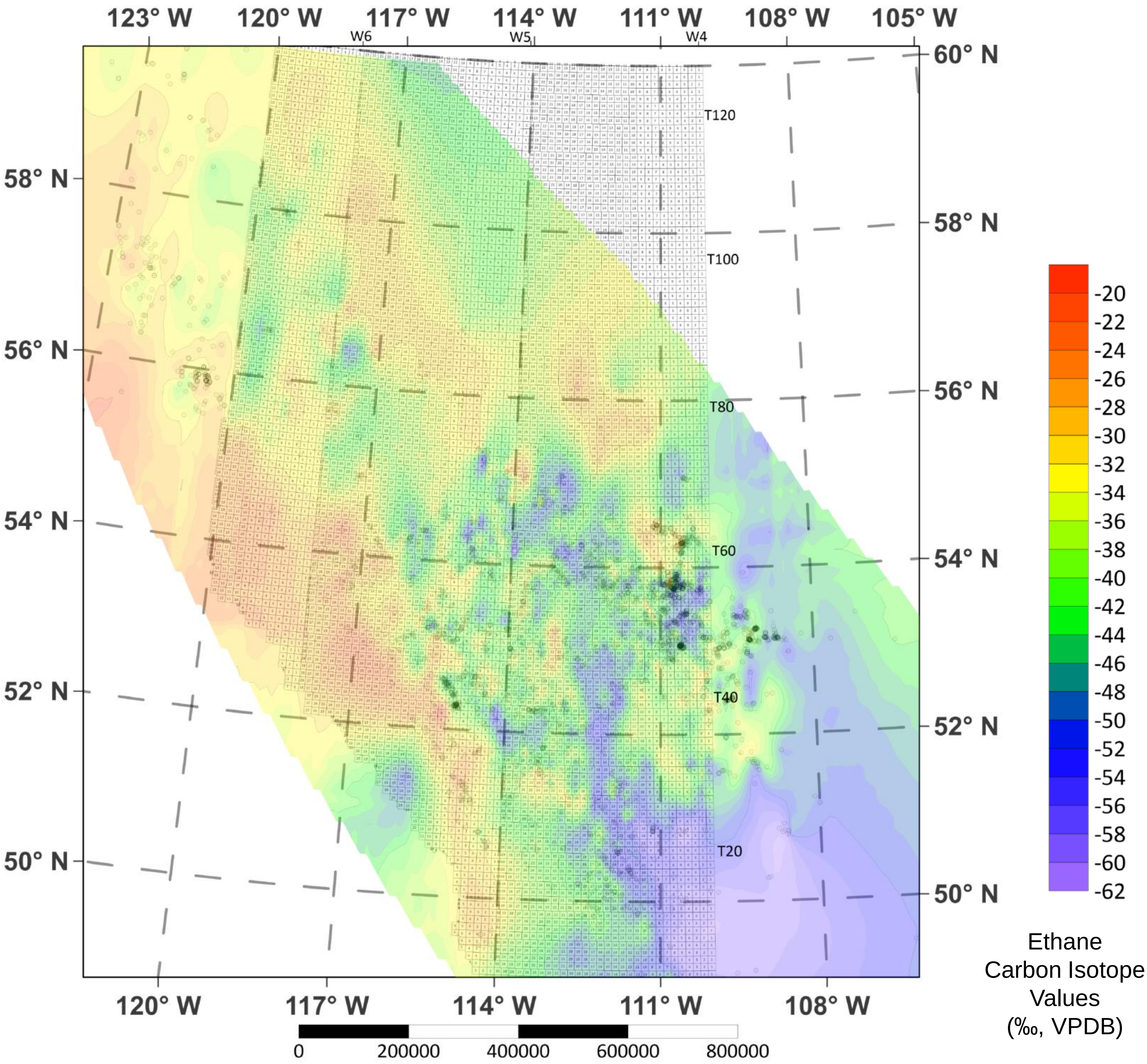


Fig. 19. Contour map of ethane carbon isotope values of surface casing vent (SCV) laid over topography

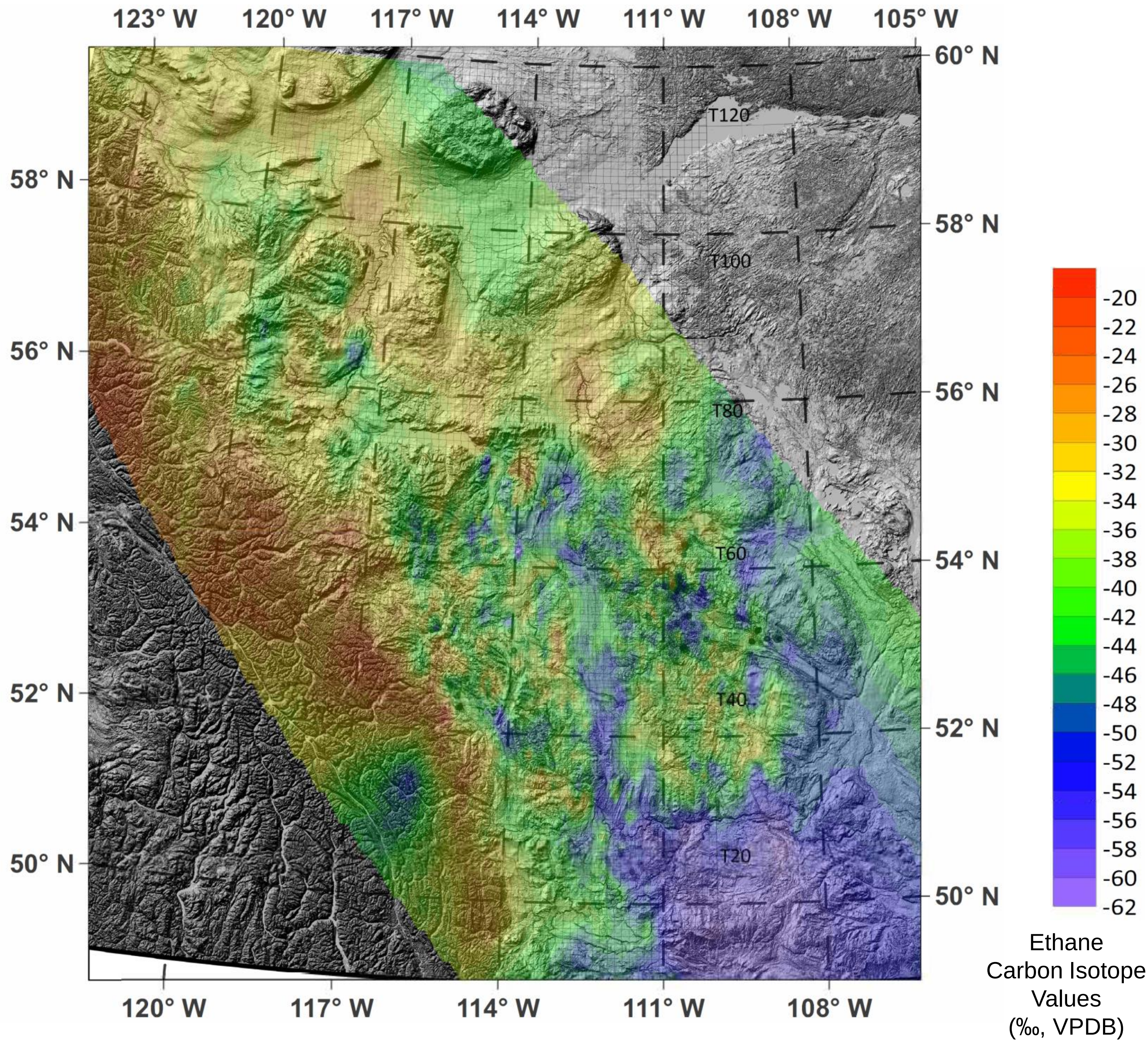


Fig. 20. Contour map of methane carbon isotope values of oil-associated production gas

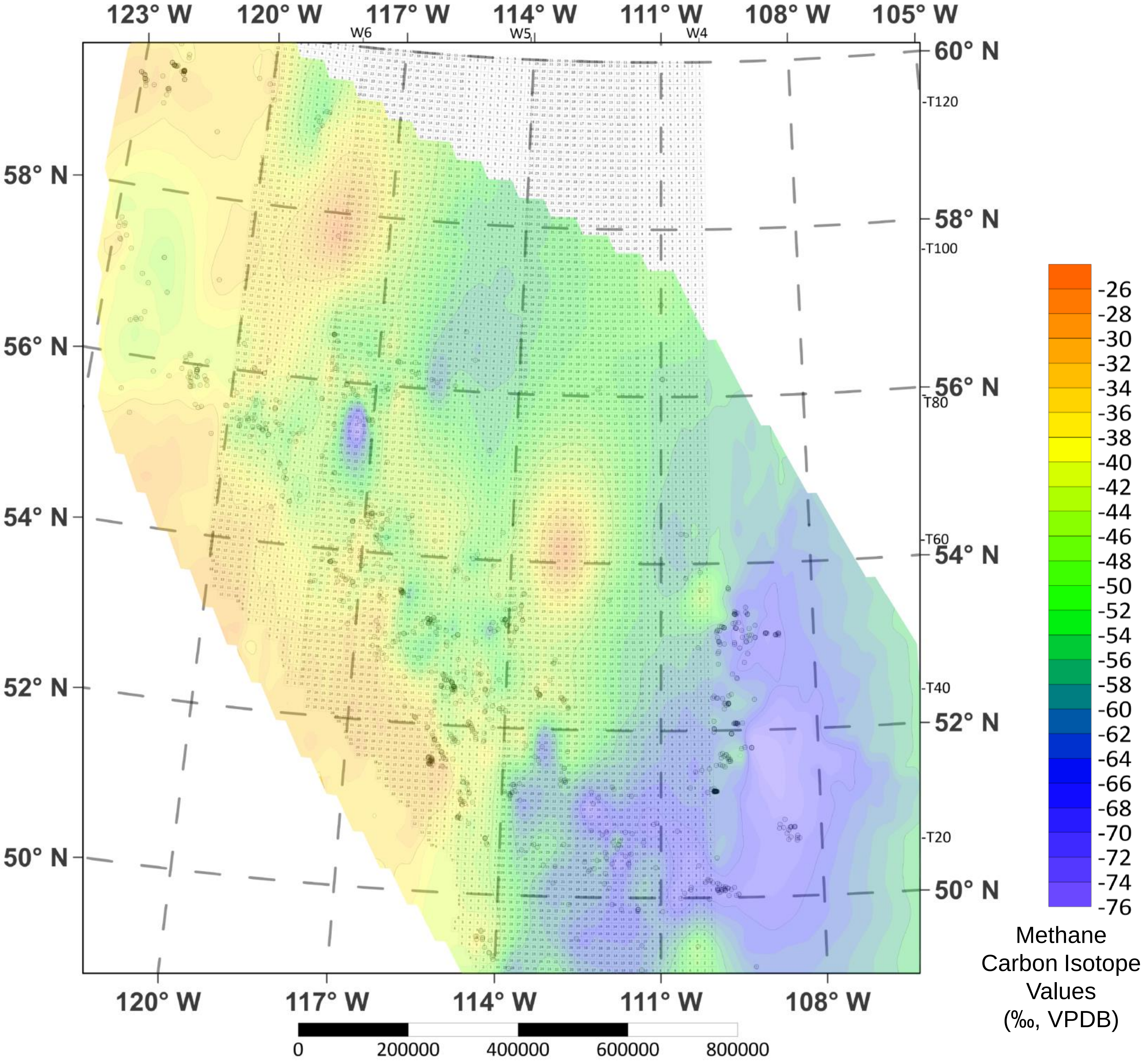


Fig. 21. Contour map of methane carbon isotope values of oil-associated production gas laid over topography

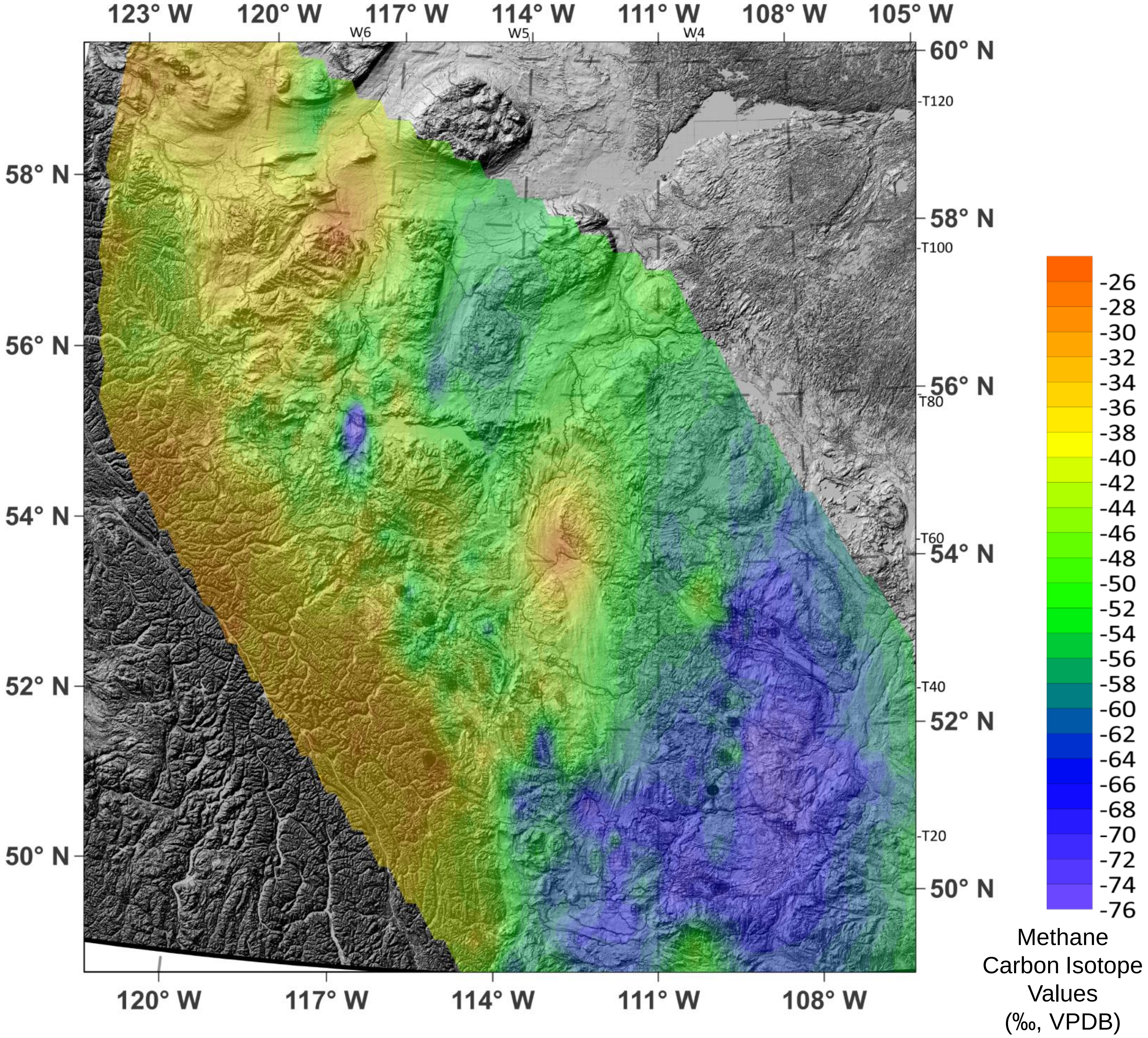


Fig. 22. Contour map of ethane carbon isotope values of oil-associated production gas

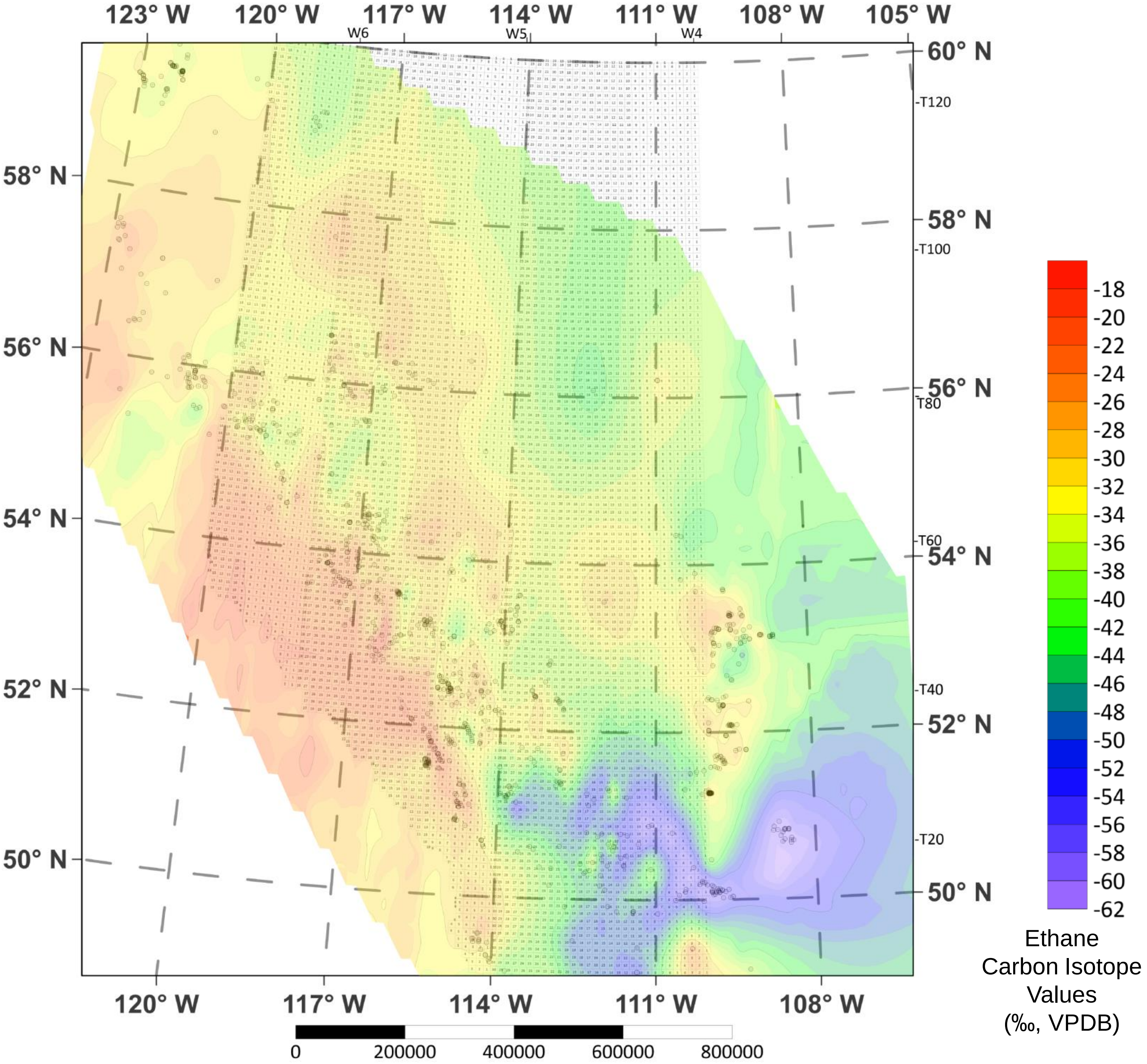


Fig. 23. Contour map of ethane carbon isotope values of oil-associated production gas laid over topography

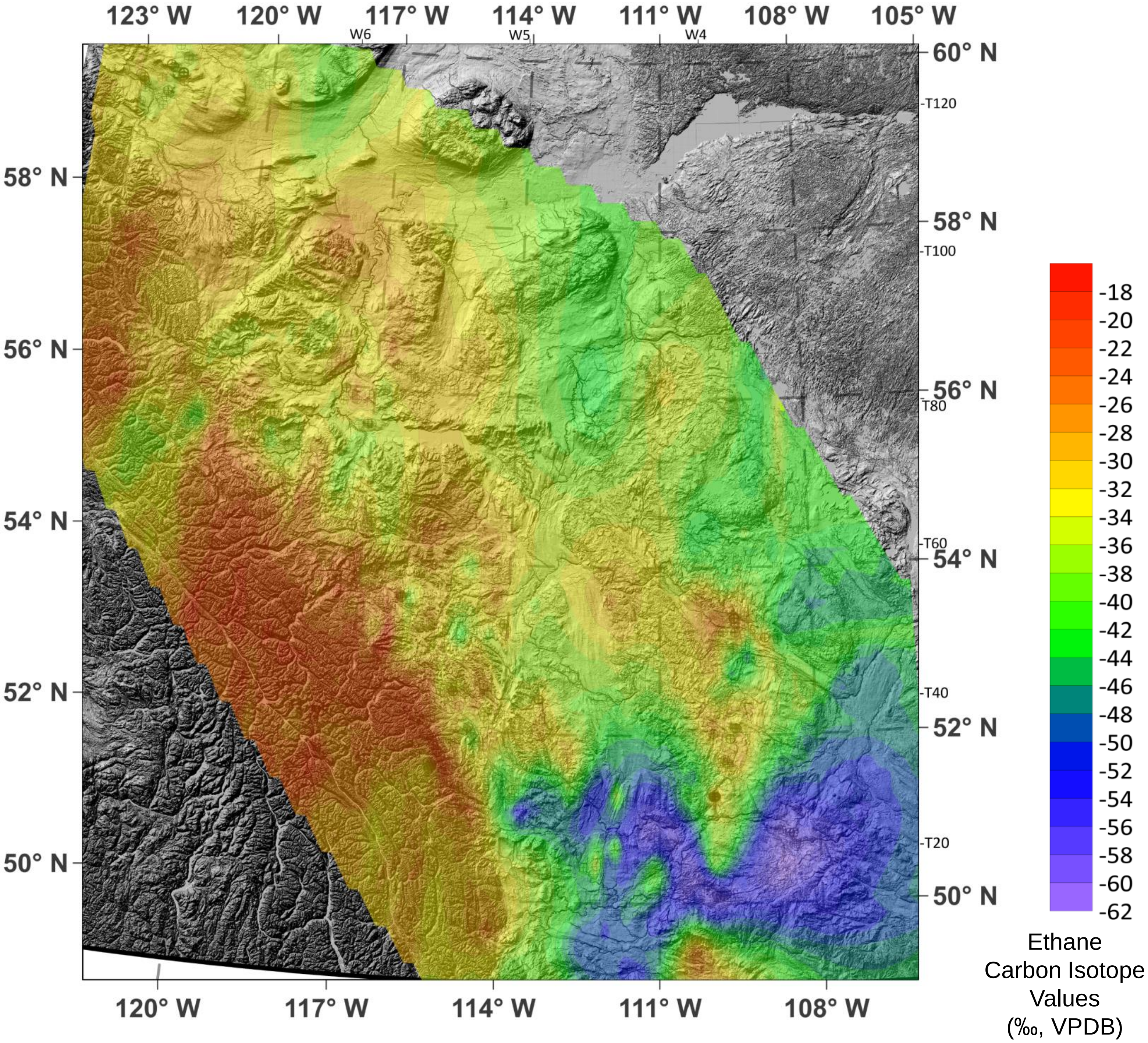


Fig. 24. Contour map of carbon dioxide carbon isotope values of oil-associated production gas

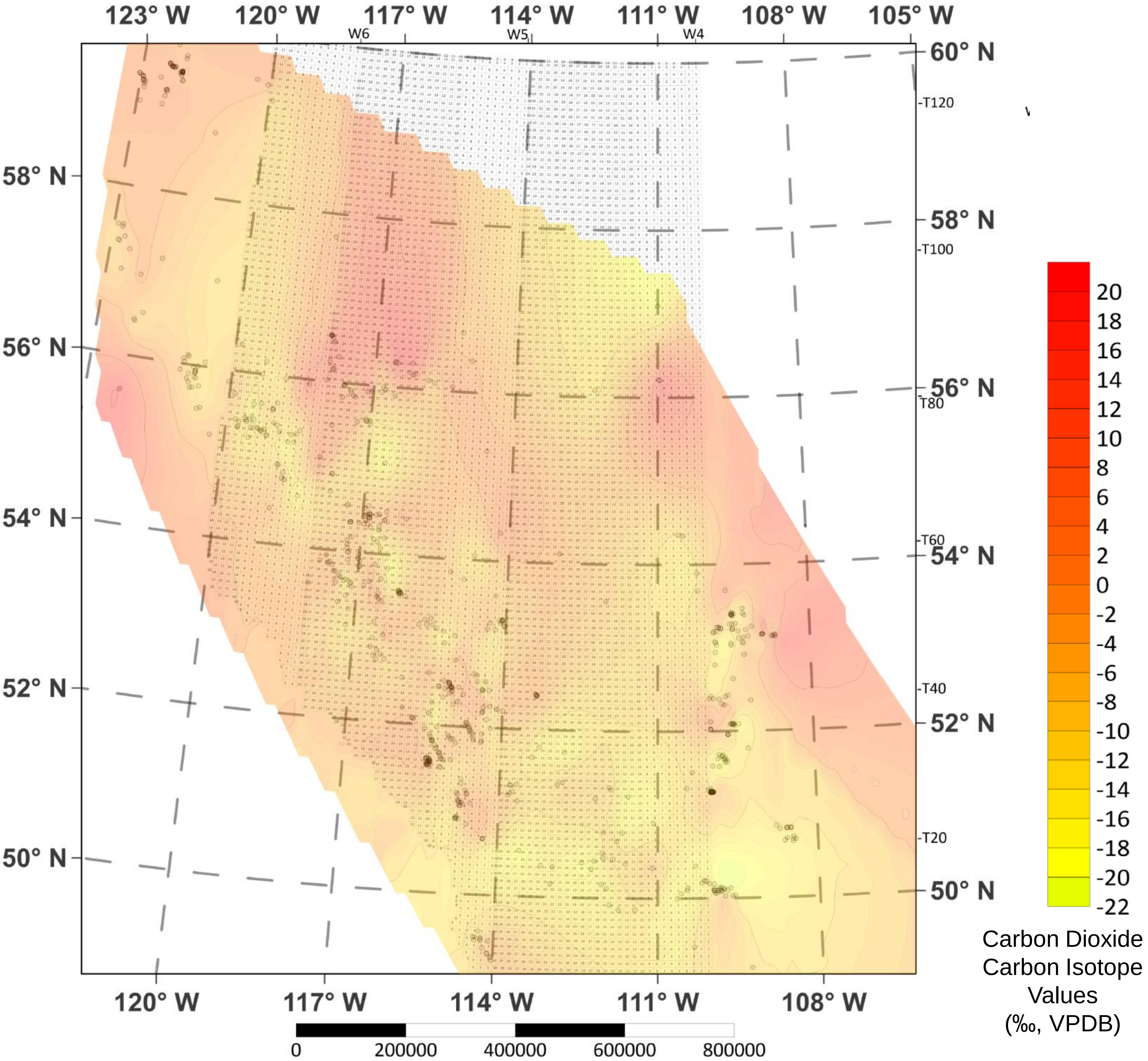


Fig. 25. Contour map of carbon dioxide carbon isotope values of oil-associated production gas laid over topography

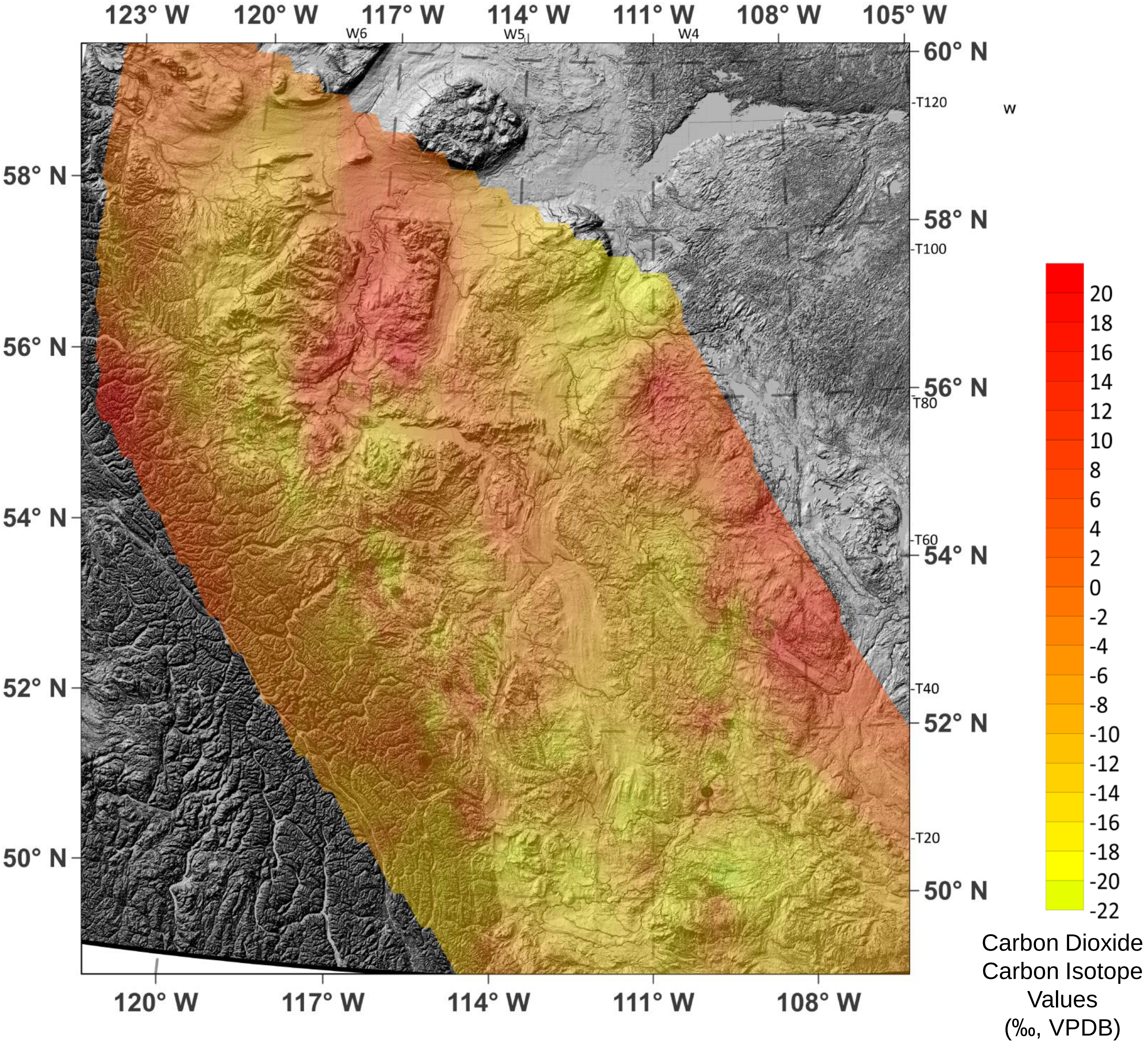


Fig. 26. Location map of sampled domestic water wells (WW), ground migration (GM) and surface casing vent (SCV) samples in a zoomed area in southwest Alberta

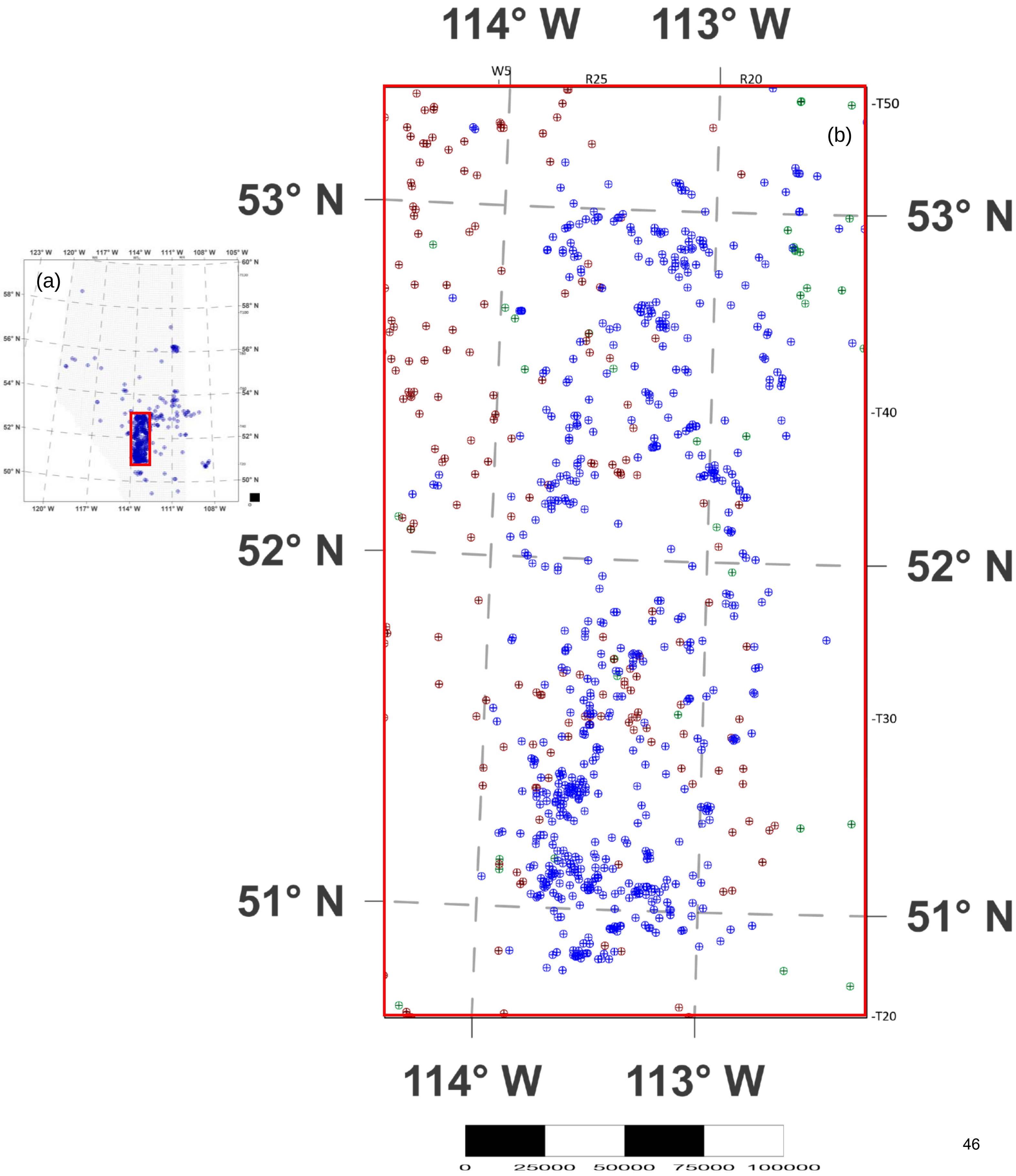


Fig. 27a. Histogram of methane (a), ethane (b) and propane (c) carbon isotopic composition measured in samples located in a zoomed area

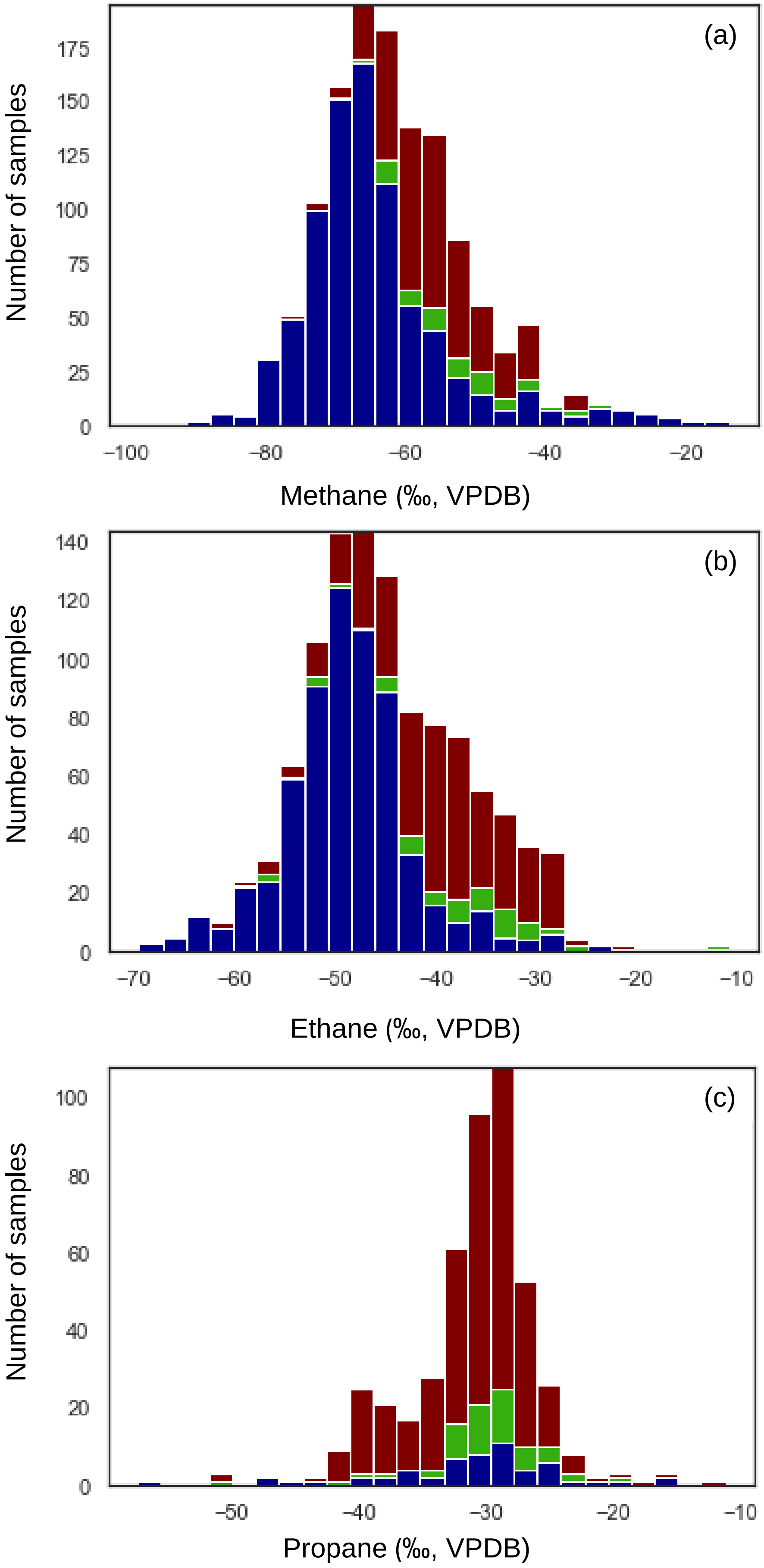


Fig. 27b. Histogram of *i*-butane, *n*-butane, and CO_2 isotopic compositions from WW (blue), GM (green), and SCV (burgundy) samples in zoomed area

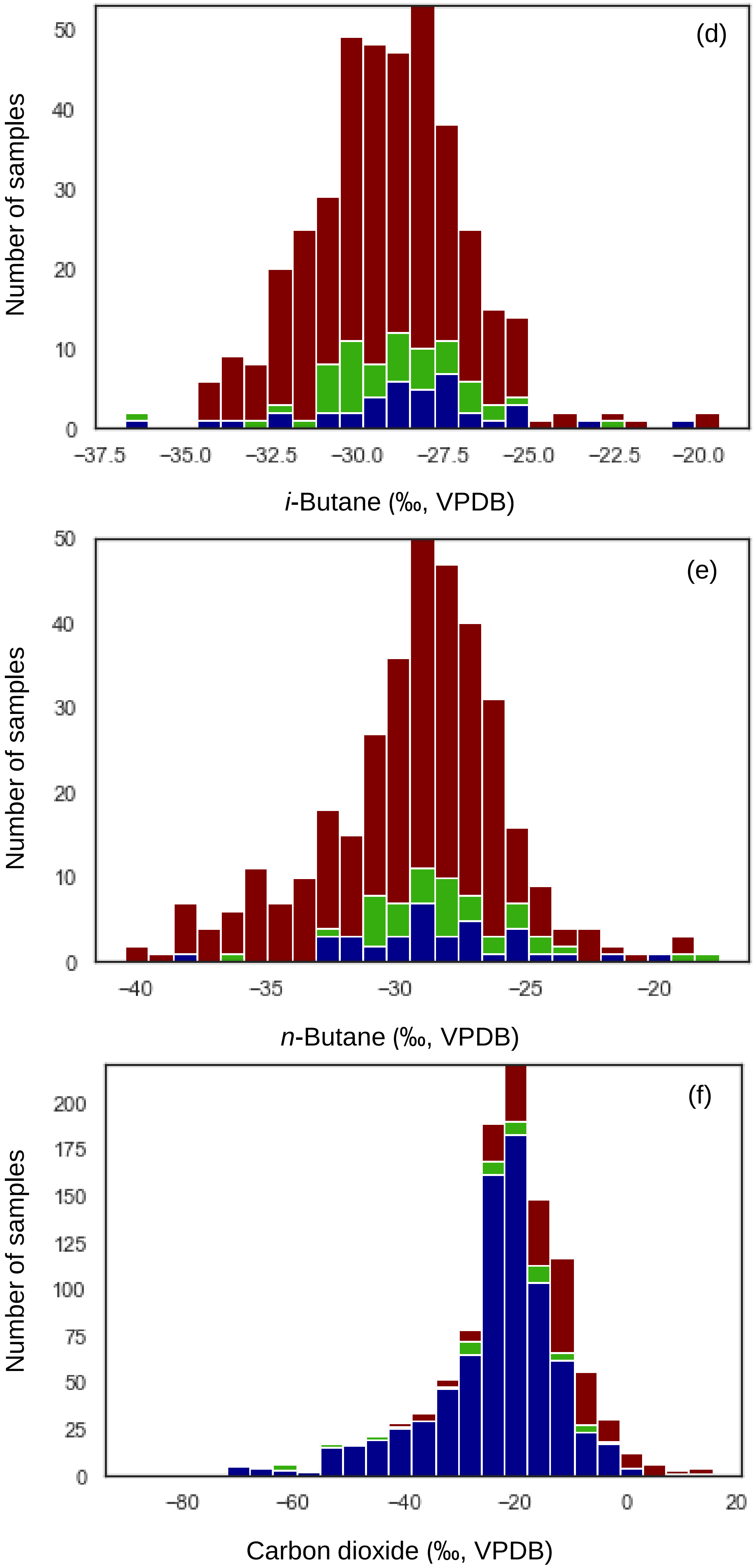


Fig. 28a. Pairplots containing histogram and cross plots of the carbon isotopic composition of methane (i, a), ethane (ii, b) and carbon dioxide (iii, c) from domestic water wells (WW), ground migration (GM), surface casing vent (SCV) and oil-associated production gas samples in a zoomed area

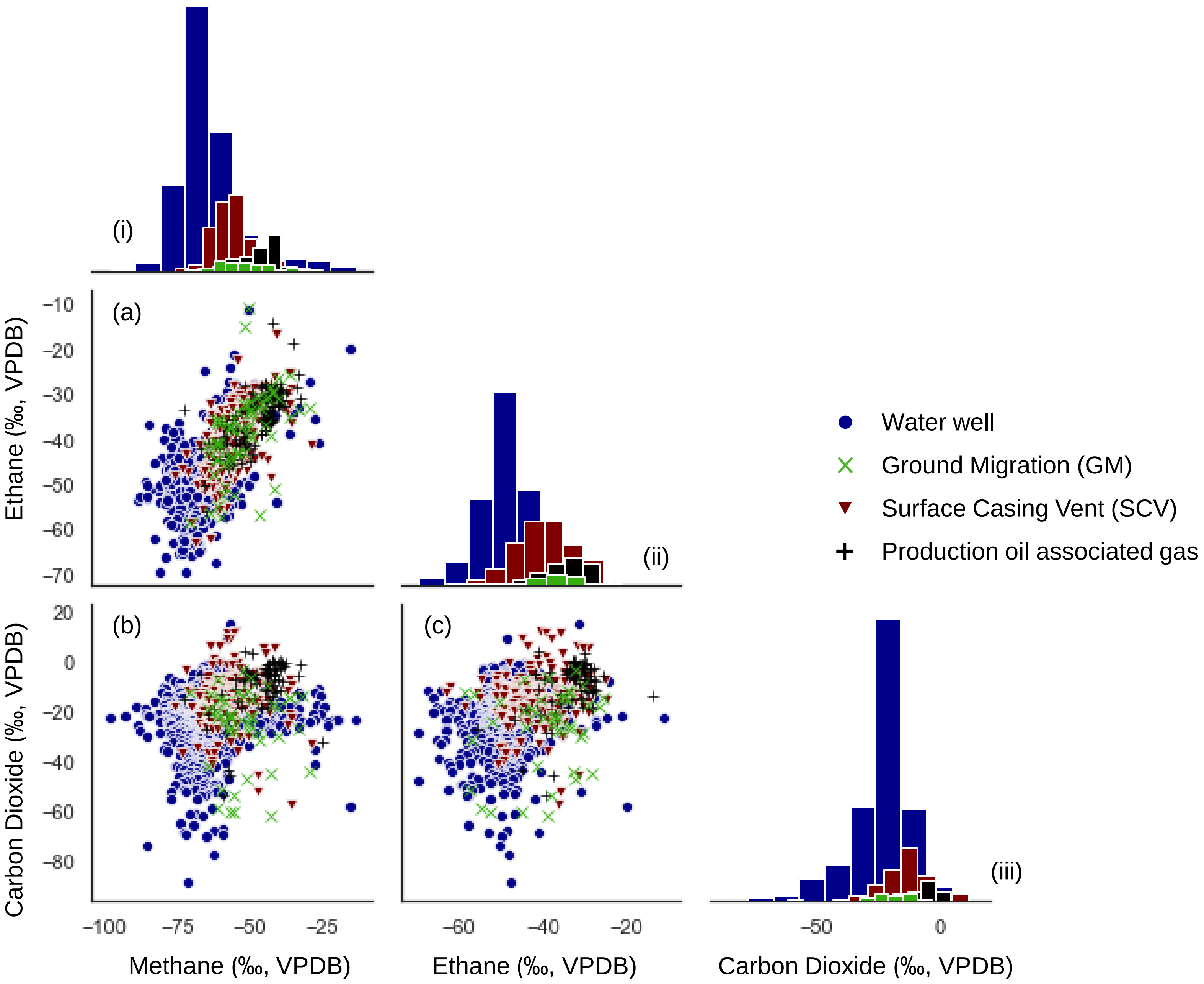


Fig. 28b. Pairplots containing histogram and cross plots of the carbon isotopic composition of ethane (i), propane (ii), *iso*-butane (iii), and *n*-butane (iv) from domestic water wells (WW), ground migration (GM), surface casing vent (SCV) and oil-associated production gas samples in a zoomed area

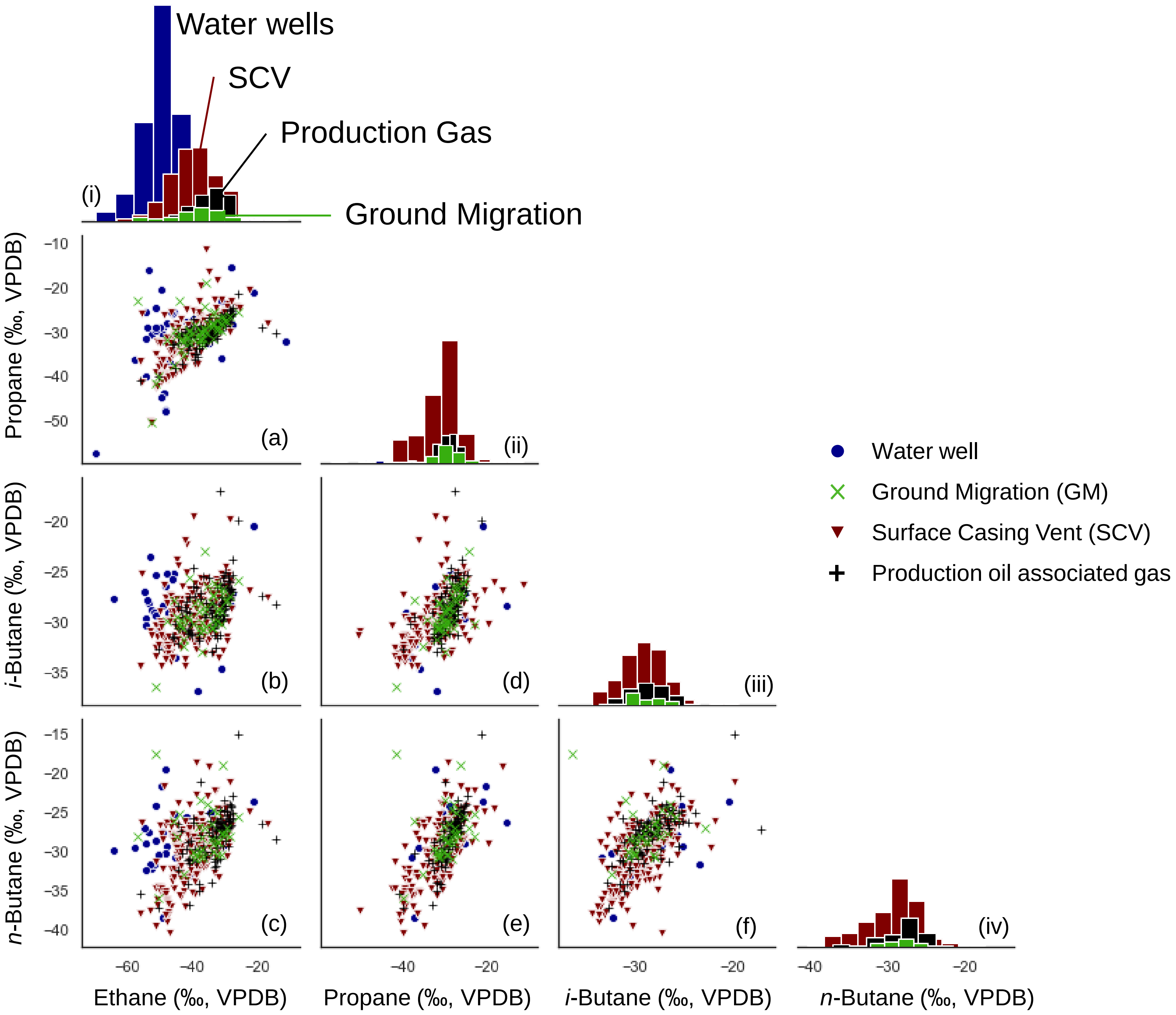


Fig. 29a. Kernel model statistical comparison of the carbon isotopic composition of methane (i), ethane (ii), propane (iii), *iso*-butane (iv), *n*-butane (v) and carbon dioxide (vi) from domestic water wells (WW) and oil-associated production gas samples in a zoomed area

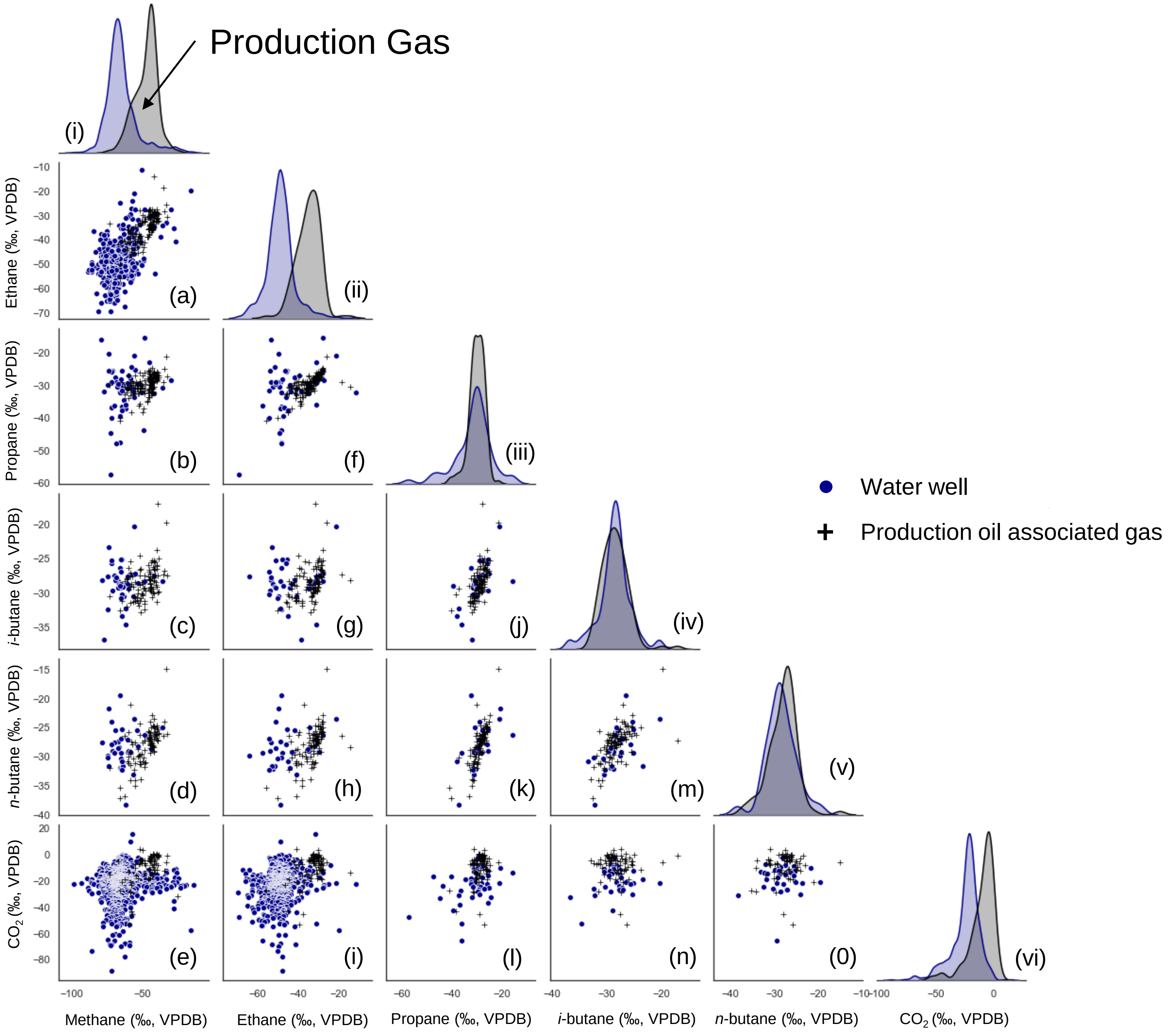


Fig. 29b. Kernel model statistical comparison of the carbon isotopic composition of methane (i), ethane (ii), propane (iii), *iso*-butane (iv), *n*-butane (v) and carbon dioxide (vi) from domestic water wells (WW) and surface casing vent (SCV) gas samples in a zoomed area

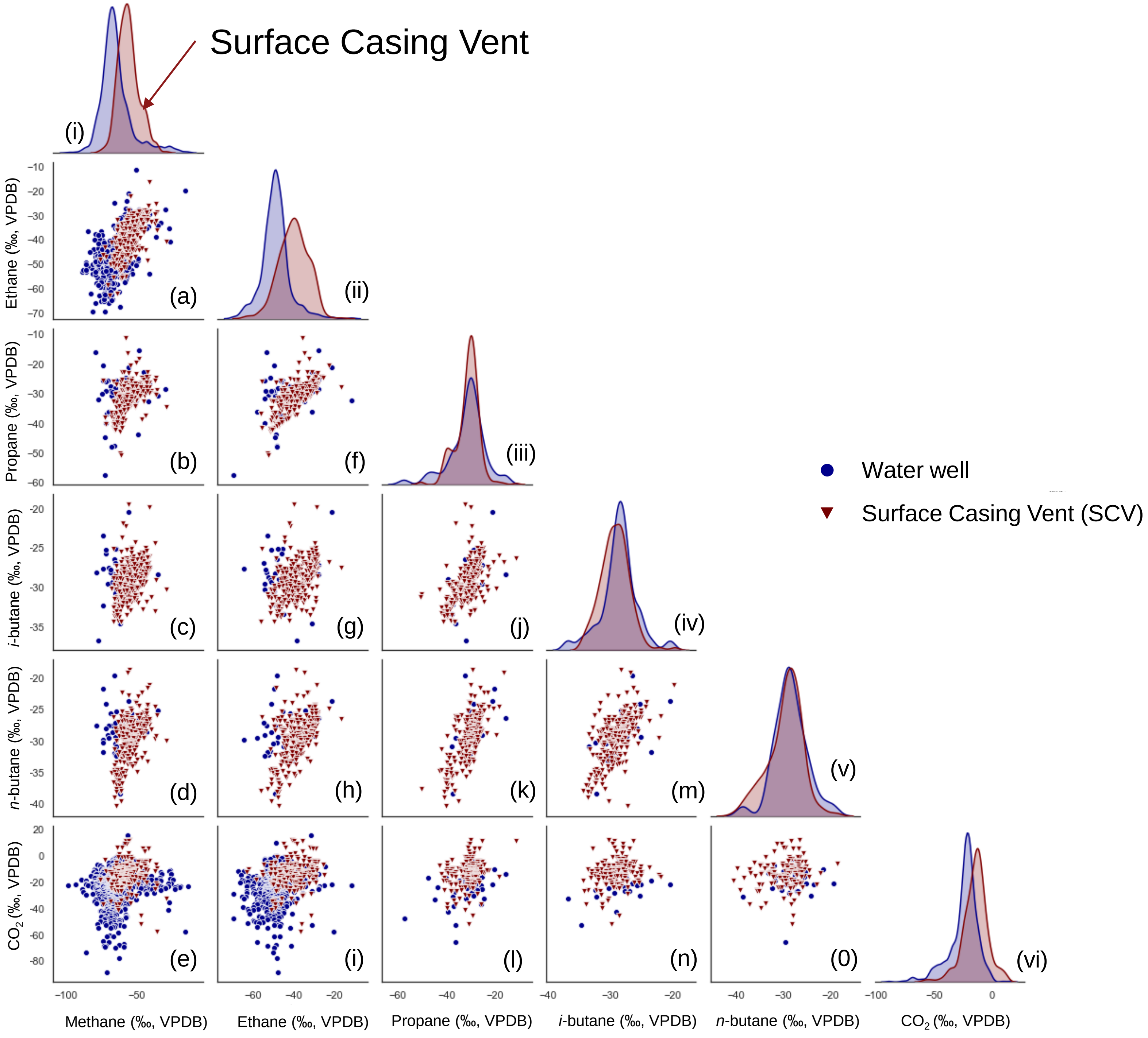


Fig. 29c. Kernel model statistical comparison of the carbon isotopic composition of methane (i), ethane (ii), propane (iii), *iso*-butane (iv), *n*-butane (v) and carbon dioxide (vi) from domestic water wells (WW) and ground migration (GM) gas samples in a zoomed area

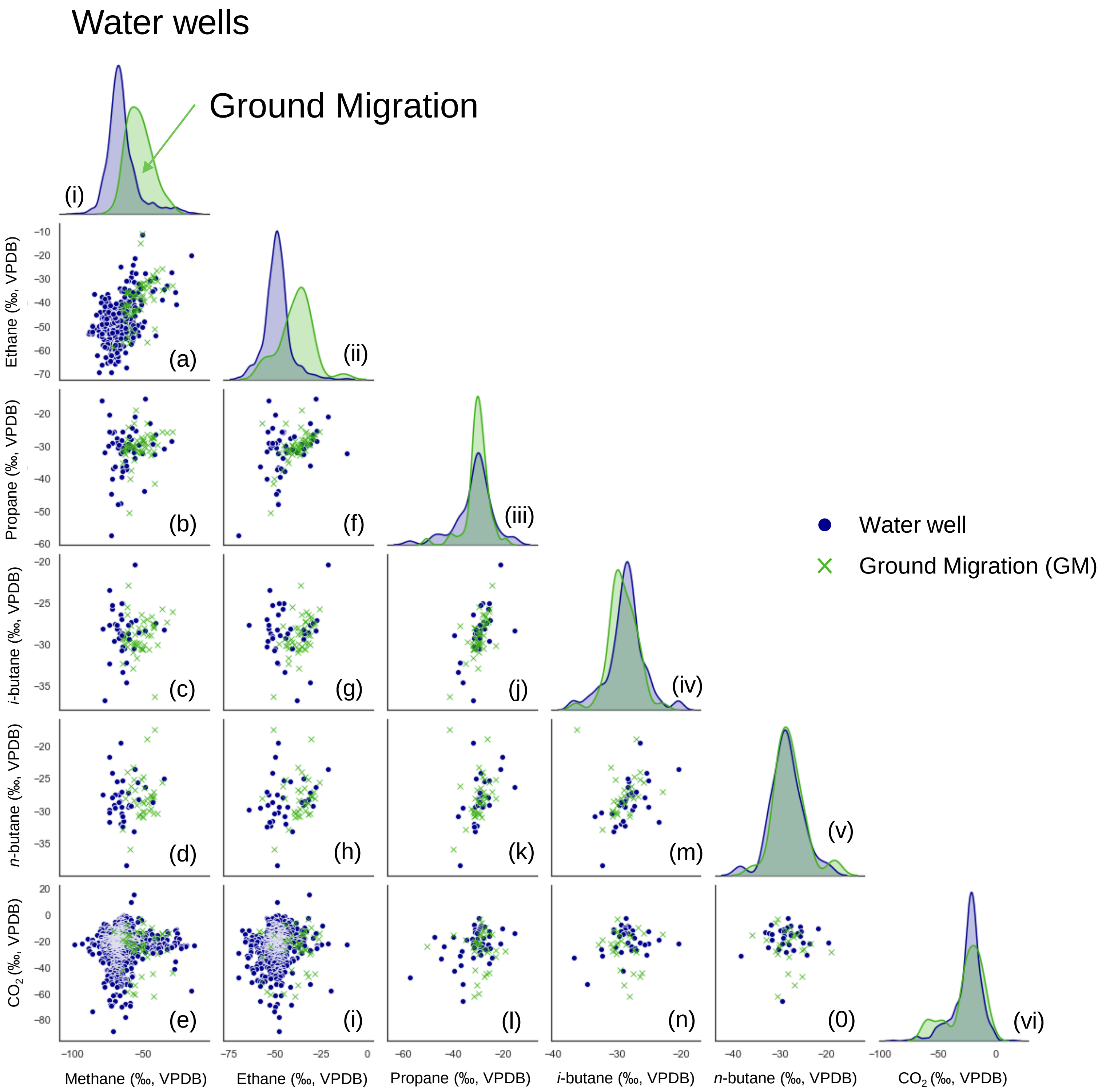


Fig. 30. Contour map of methane isotopic composition from domestic water wells (WW) in a zoomed-in area in southeast Alberta

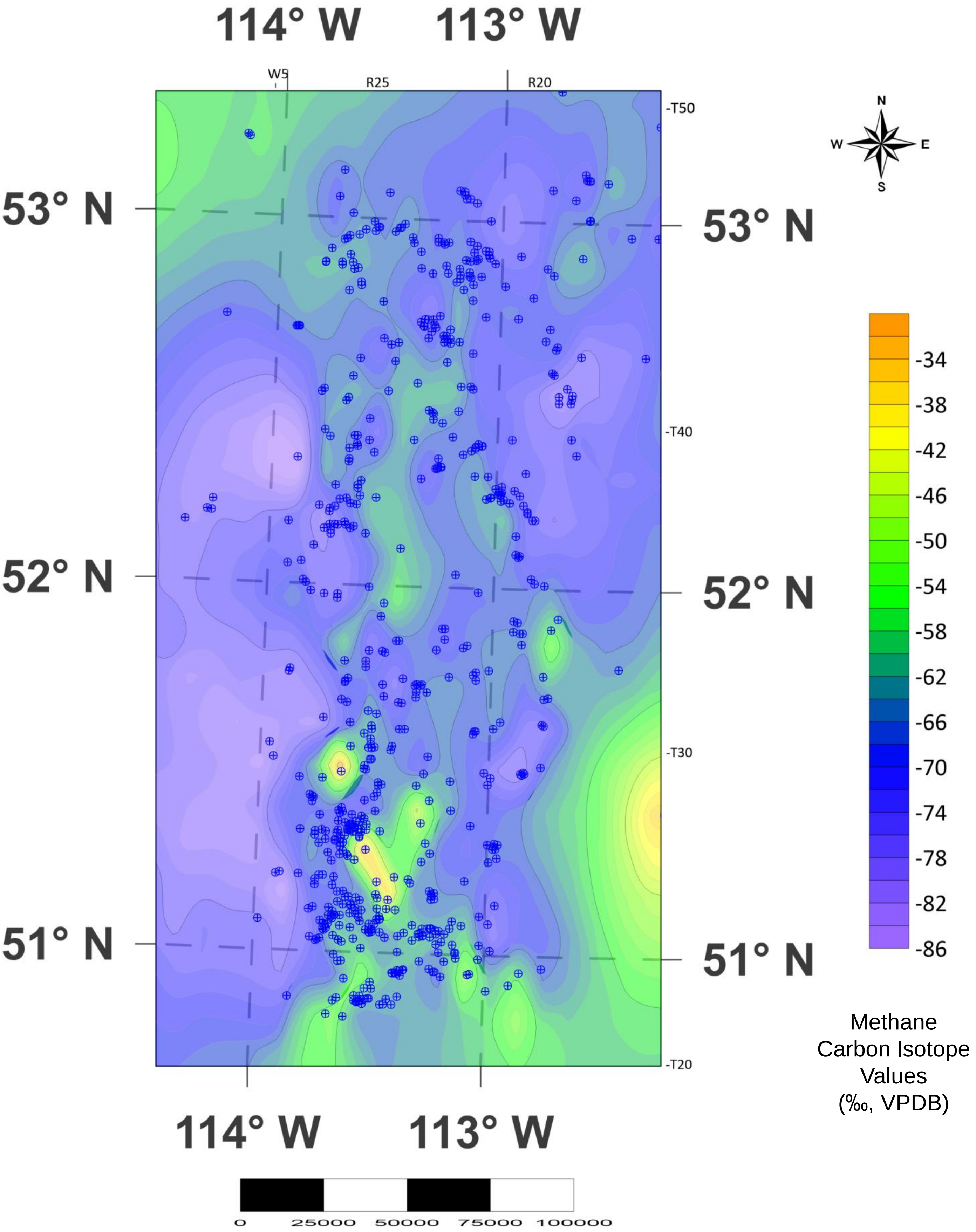


Fig. 31. Contour map of methane isotopic composition from domestic water wells (WW) overlaid topography in a zoomed-in area in southeast Alberta

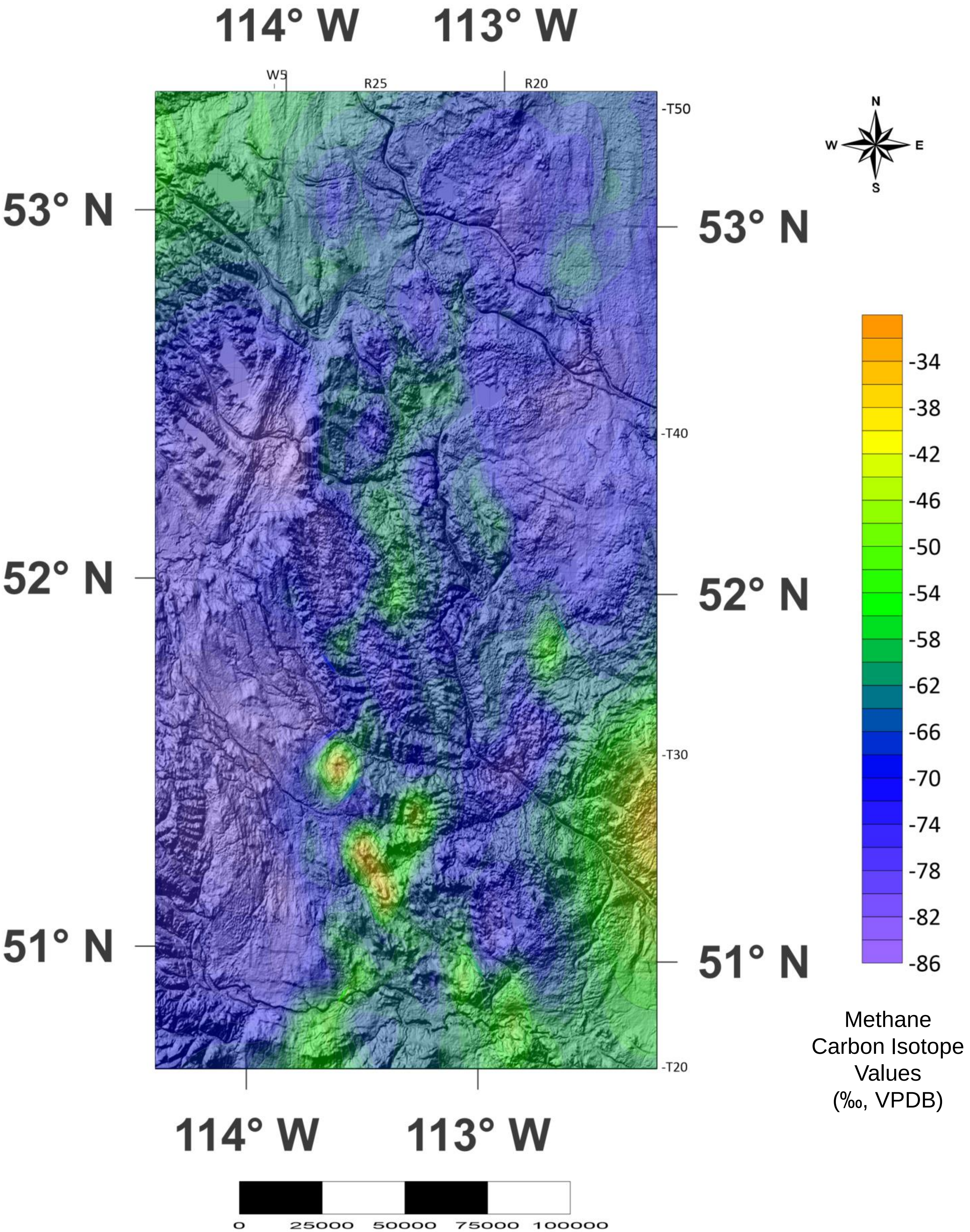


Fig. 32. Contour map of ethane isotopic composition from domestic water wells (WW) in a zoomed-in area in southeast Alberta

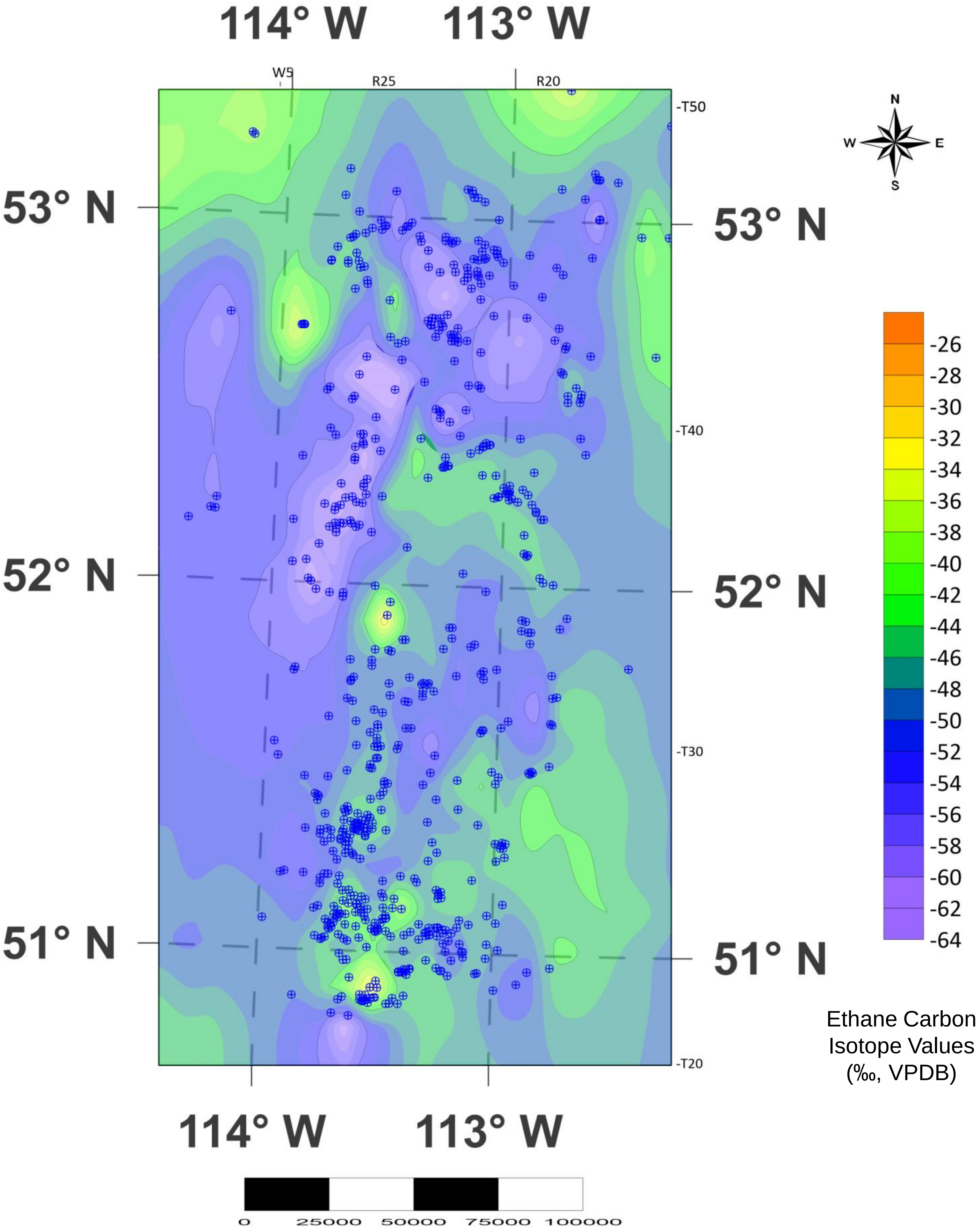


Fig. 33. Contour map of ethane isotopic composition from domestic water wells (WW) overlaid topography in a zoomed-in area in southeast Alberta

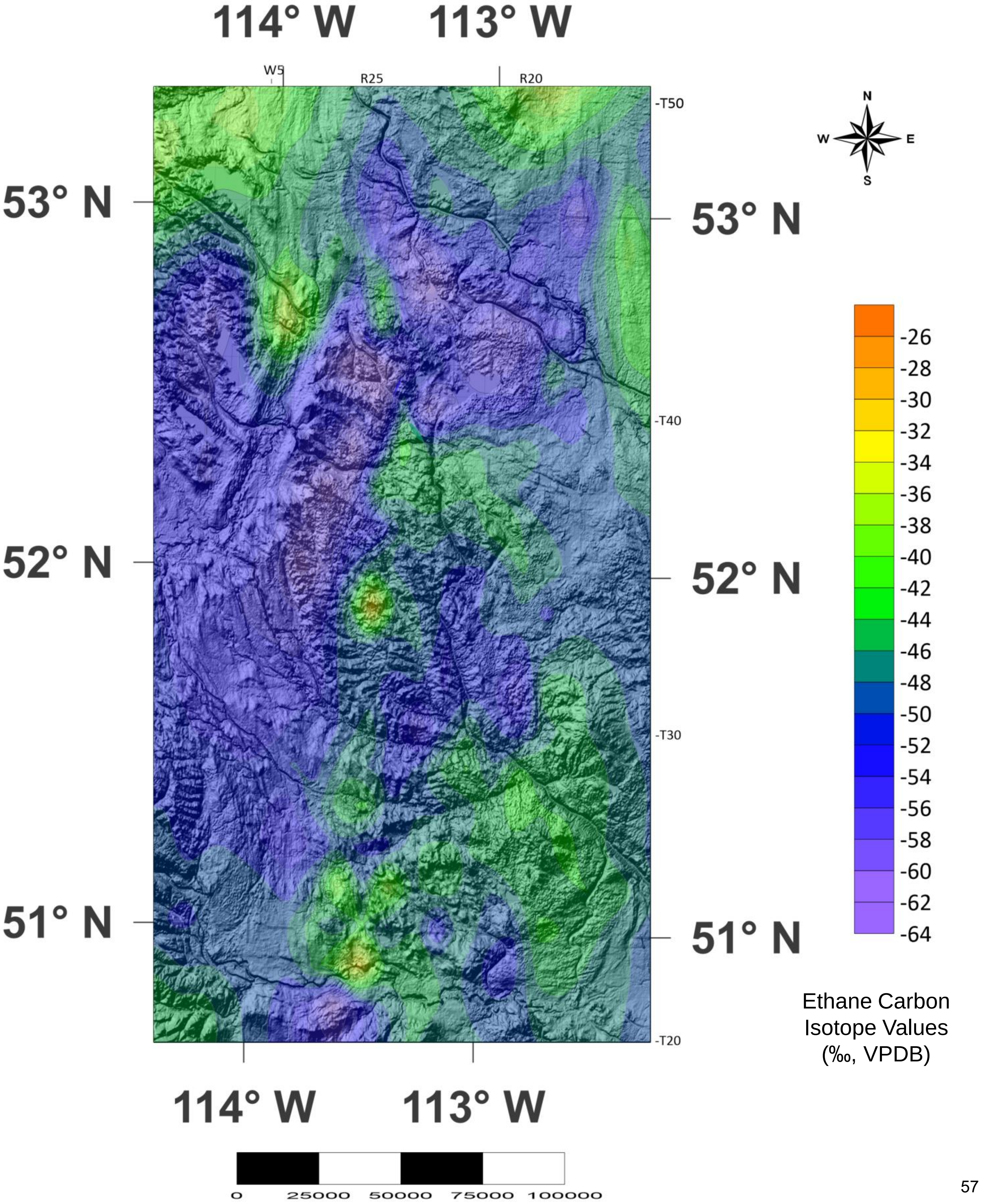


Fig. 34. Contour map of carbon dioxide isotopic composition from domestic water wells (WW) in a zoomed-in area in southeast Alberta

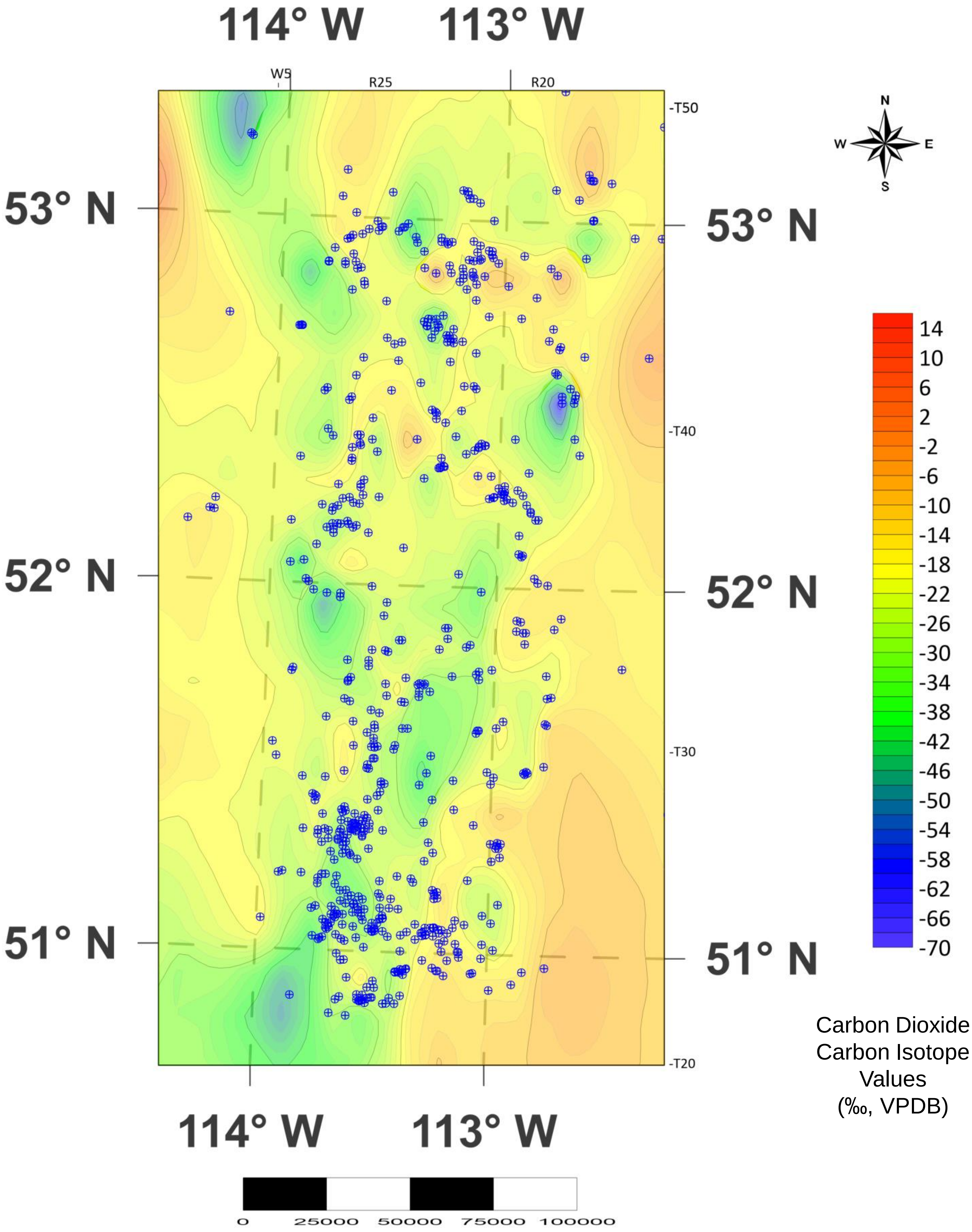


Fig. 35. Contour map of carbon dioxide isotopic composition from domestic water wells (WW) laid over topography in a zoomed-in area in southeast Alberta

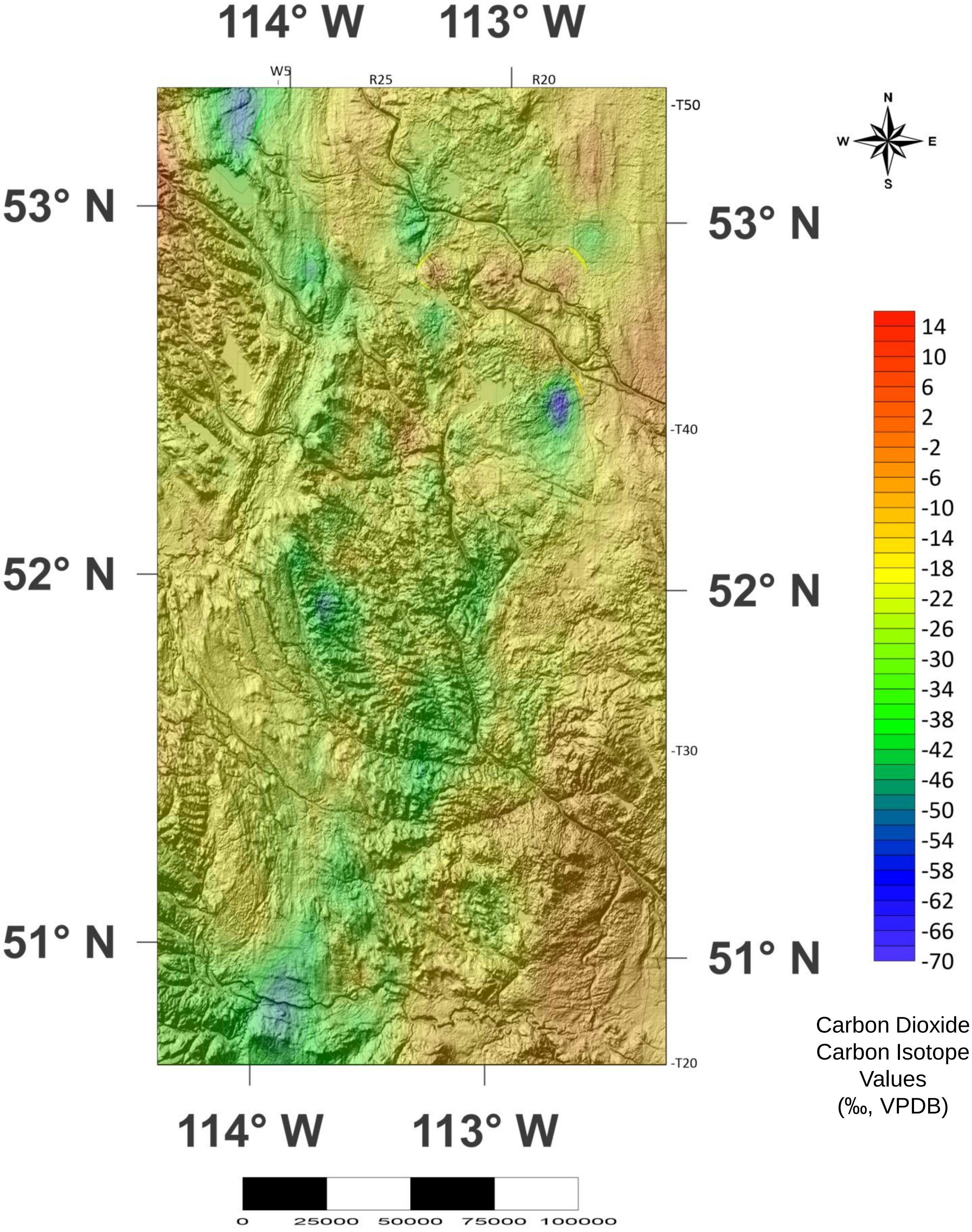


Fig. 36a. Propane isotopic composition of individual domestic water wells (WW) in the zoomed area

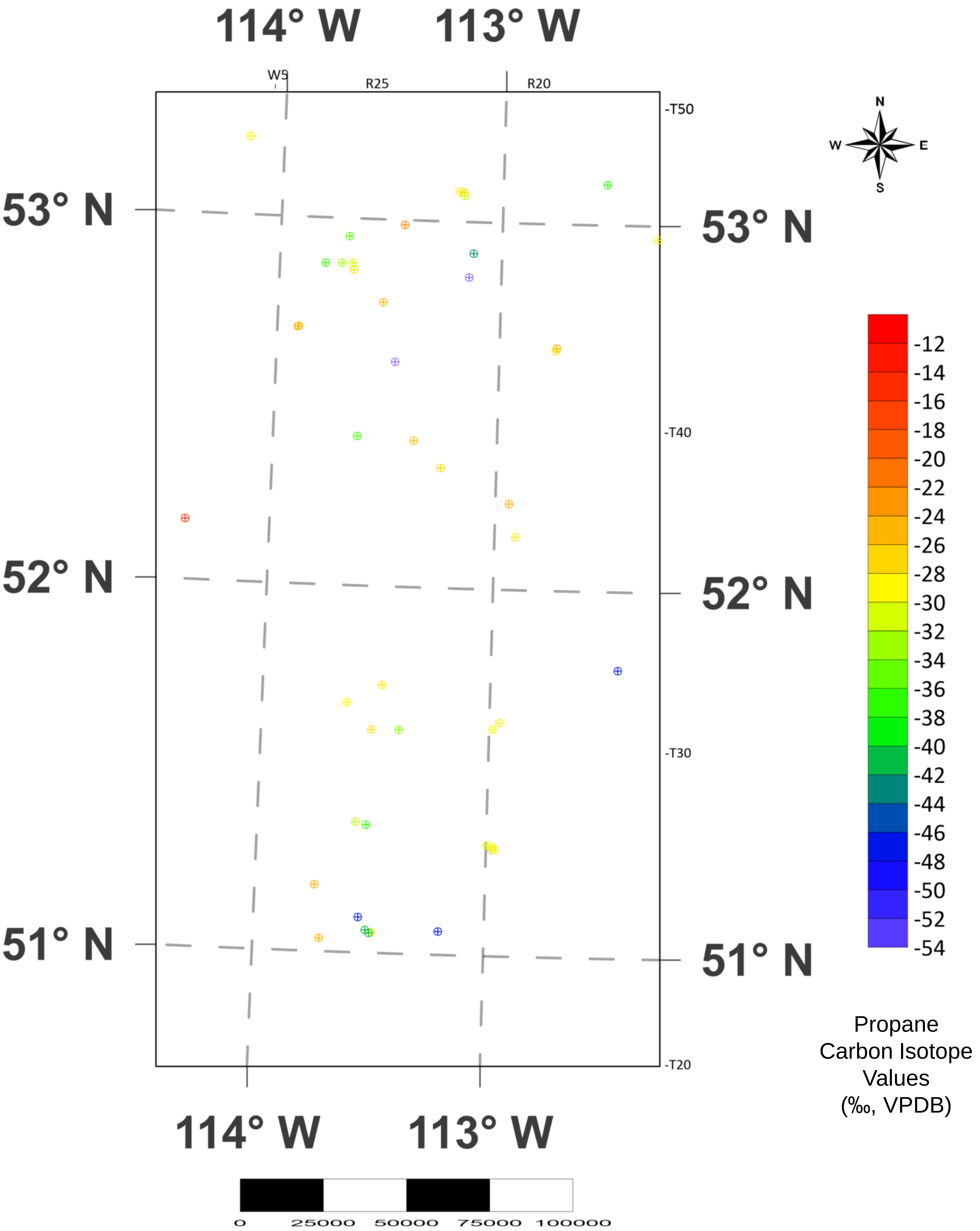


Fig. 36b. *i*-Butane isotopic composition of individual domestic water wells (WW) in the zoomed area

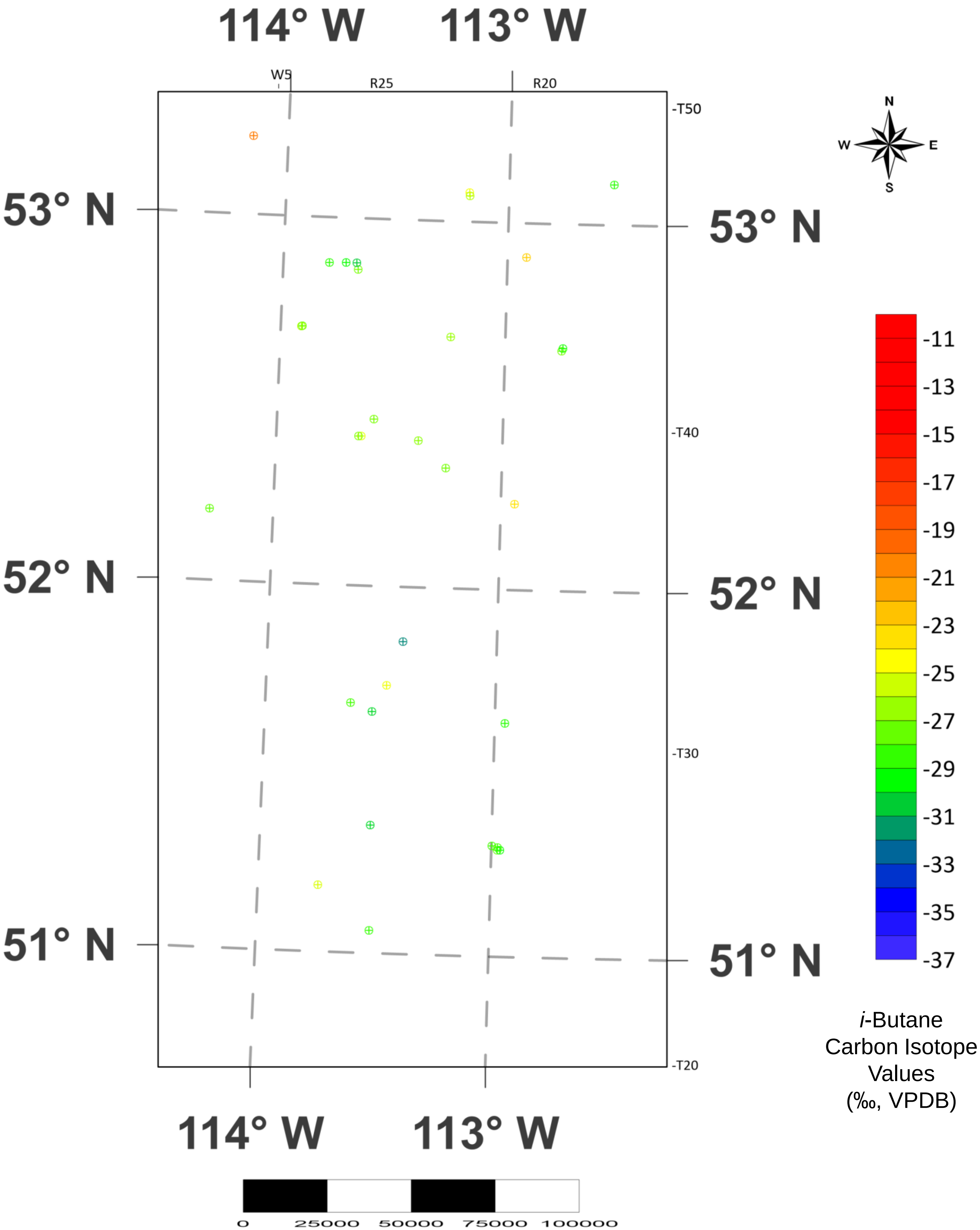


Fig. 36c. *n*-Butane isotopic composition of individual domestic water wells (WW) in the zoomed area

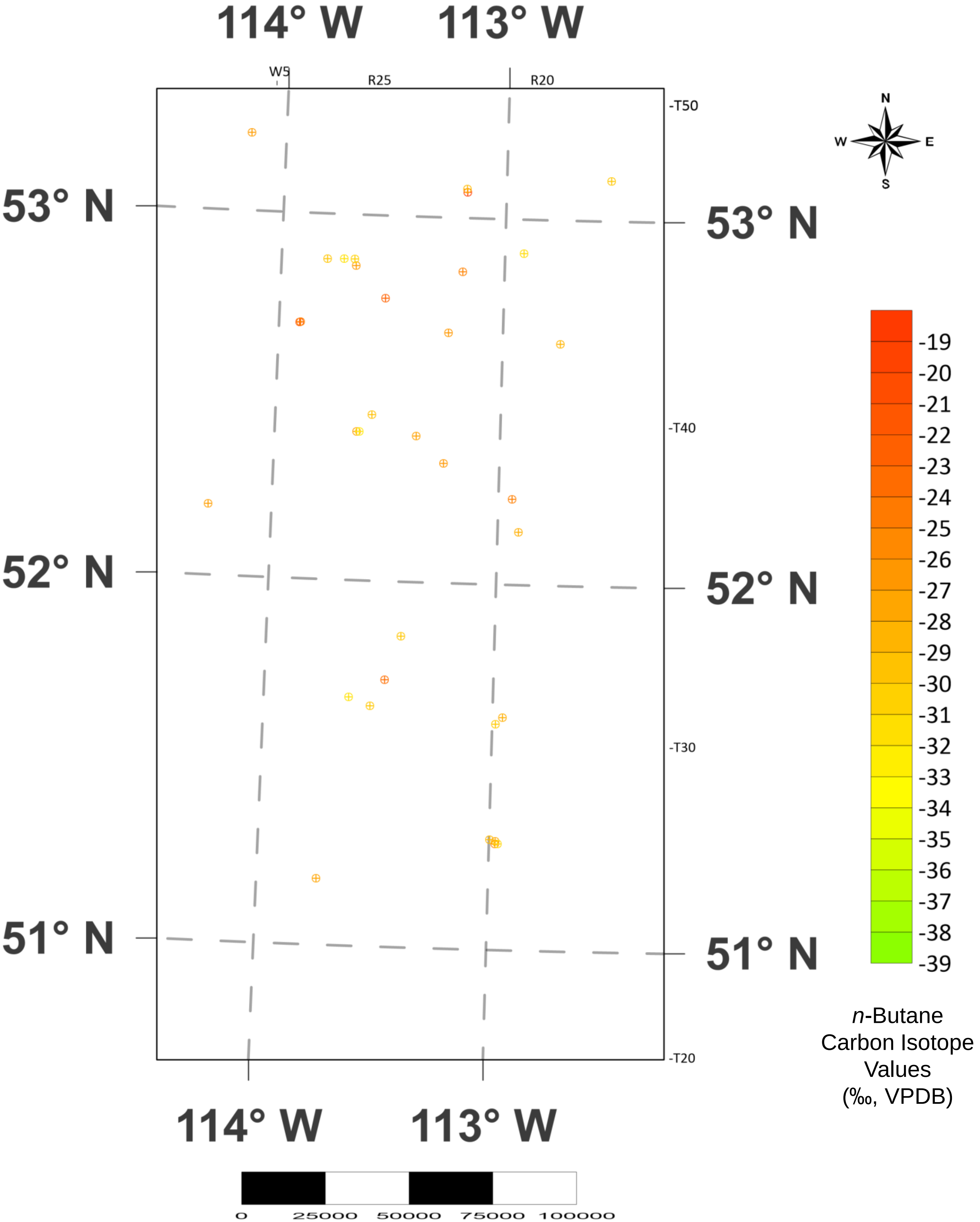


Fig. 37. Map of zoomed area showing the location of profiles and domestic water wells (WW), ground migration (GM) and surface casing vent (SCV) samples location

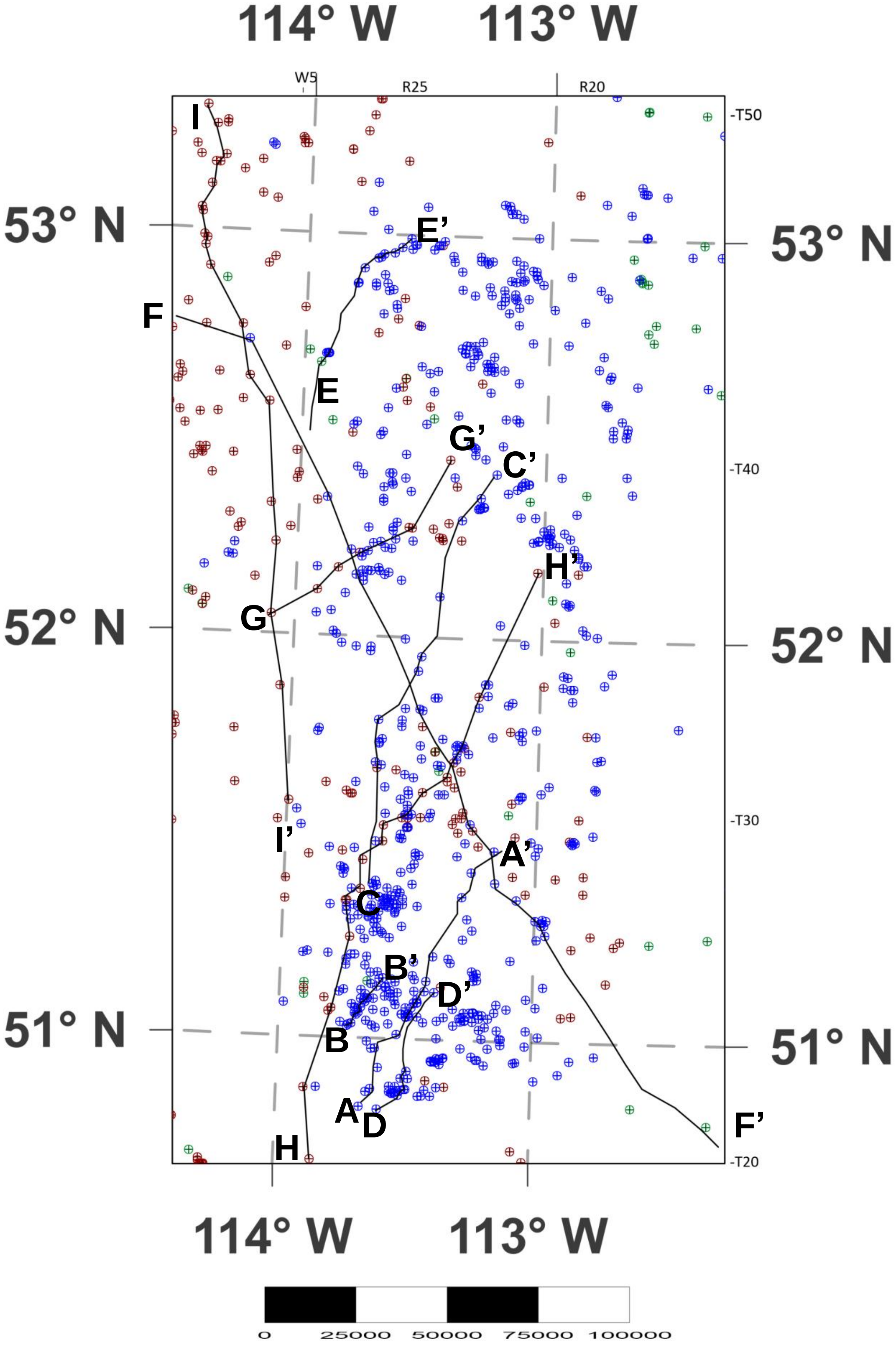


Fig. 38. Topographic cross section (a), methane (b) and ethane (c) isotopic composition profiles from A to A'

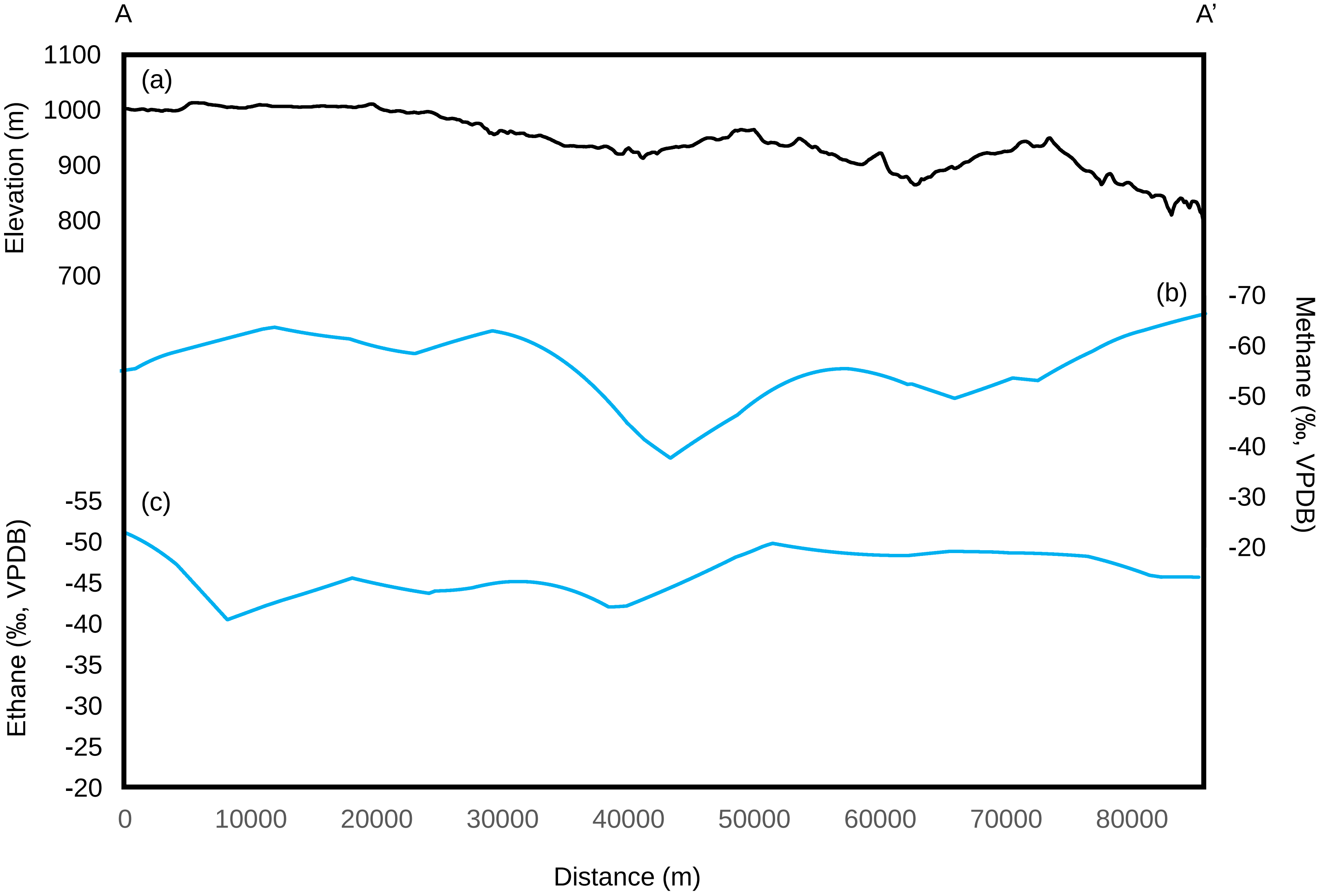


Fig. 39. Topographic cross section (a), methane (b) and ethane (c) isotopic composition profiles from B to B'

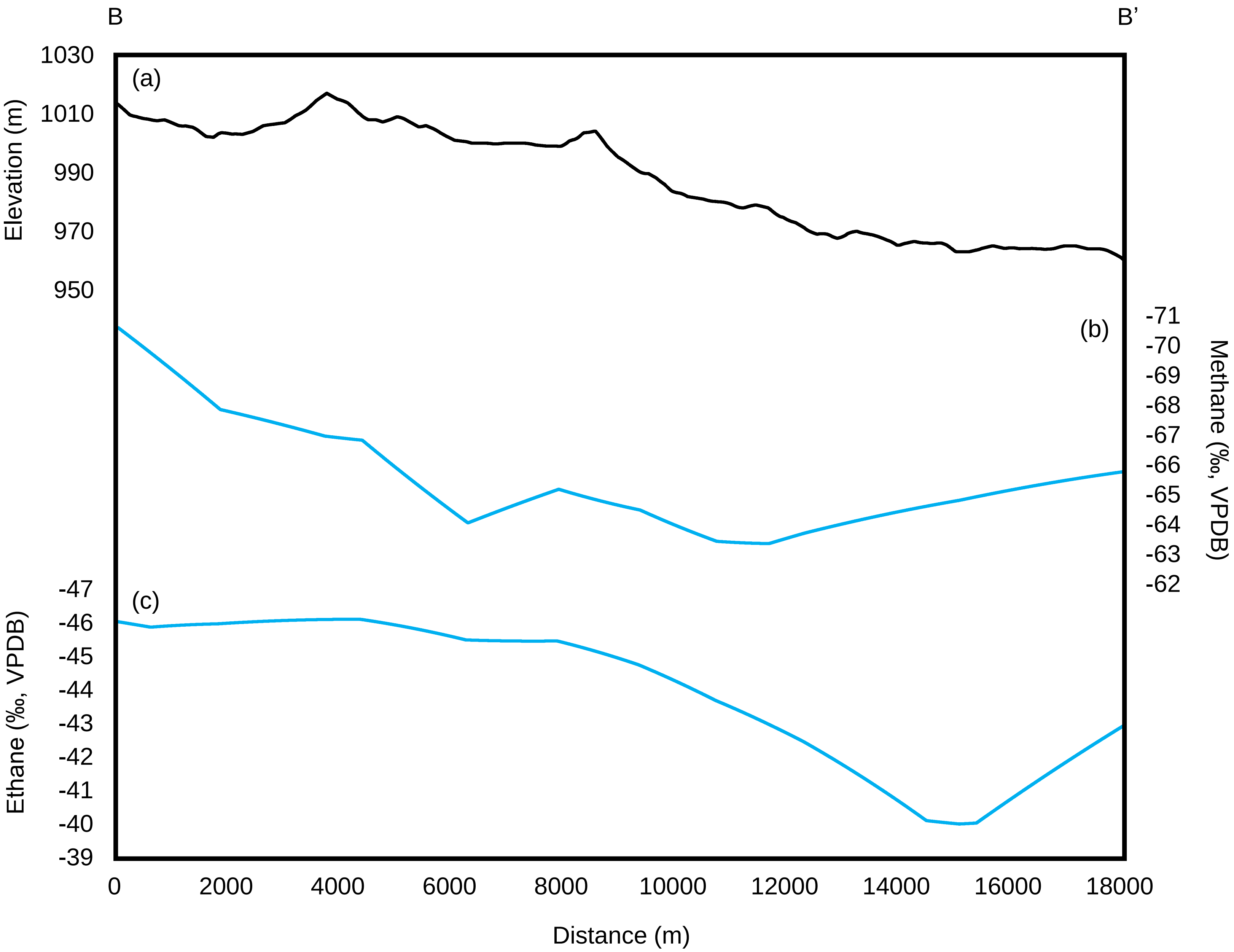


Fig. 40. Topographic cross section (a), methane (b) and ethane (c) isotopic composition profiles from C to C’

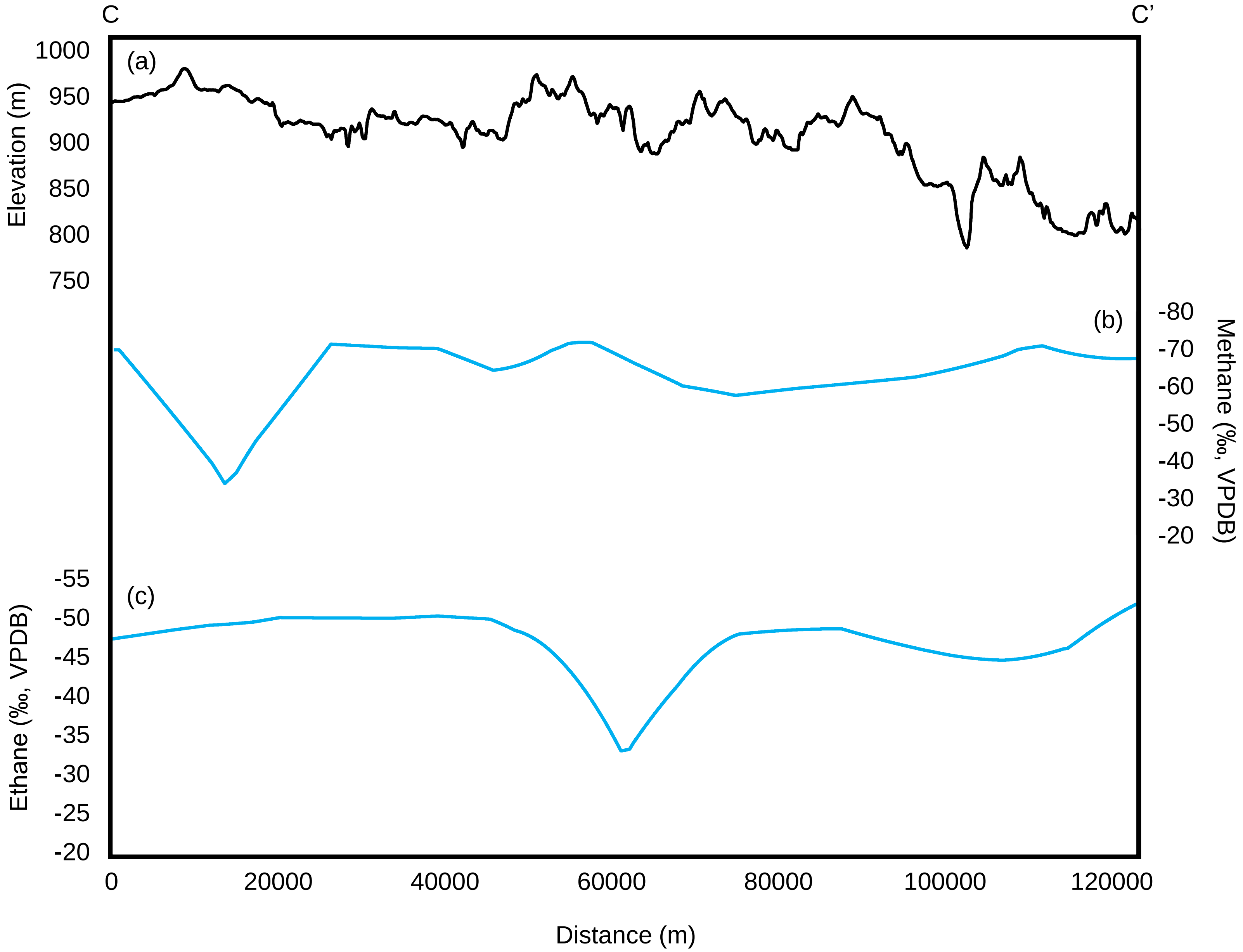


Fig. 41. Topographic cross section (a), methane (b), ethane (c) and carbon dioxide (d) isotopic composition profiles from E to E’

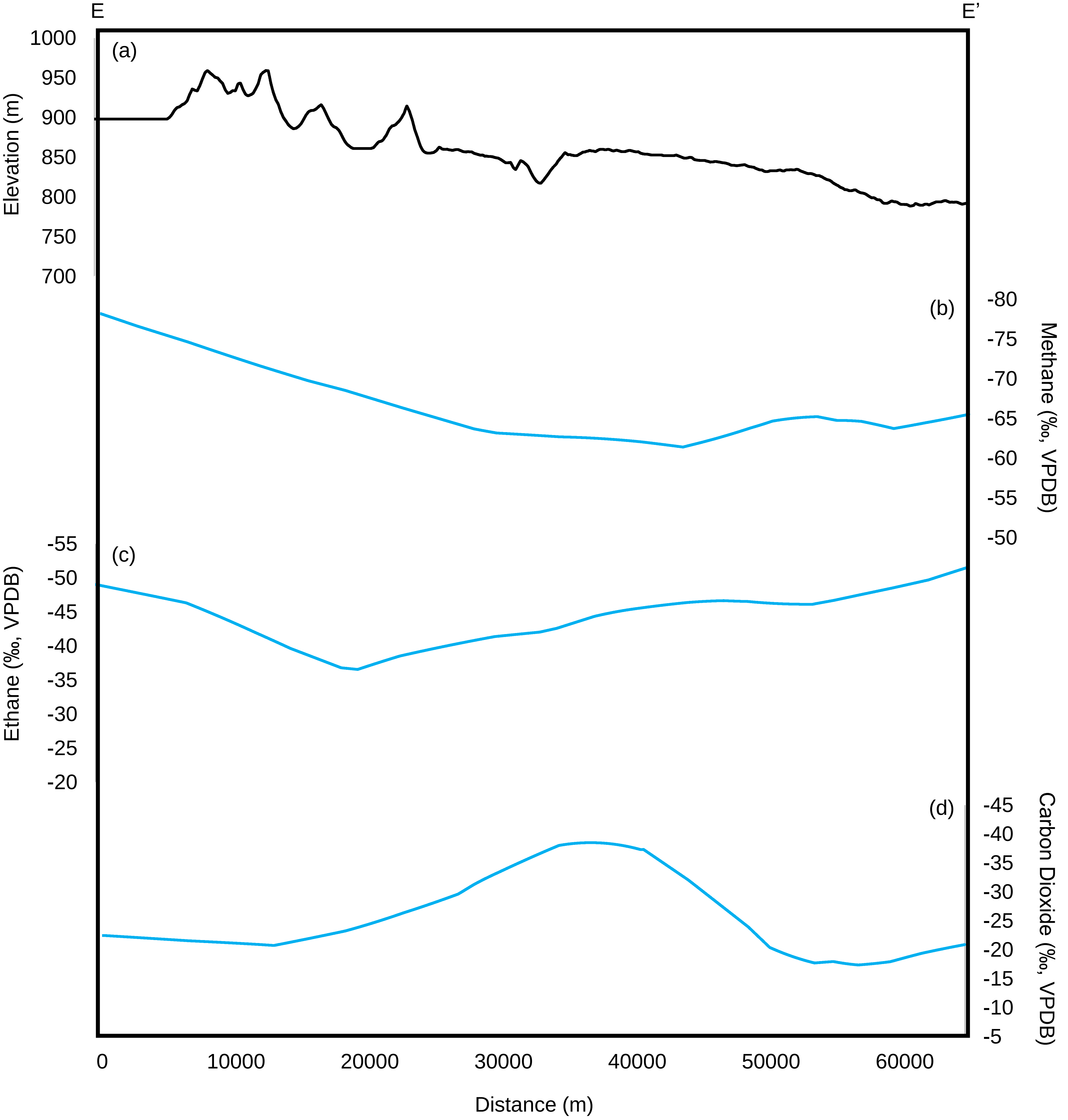


Fig. 42a. Topographic cross section (a), methane (b), ethane (c) and carbon dioxide (d) isotopic composition profiles from G to G’

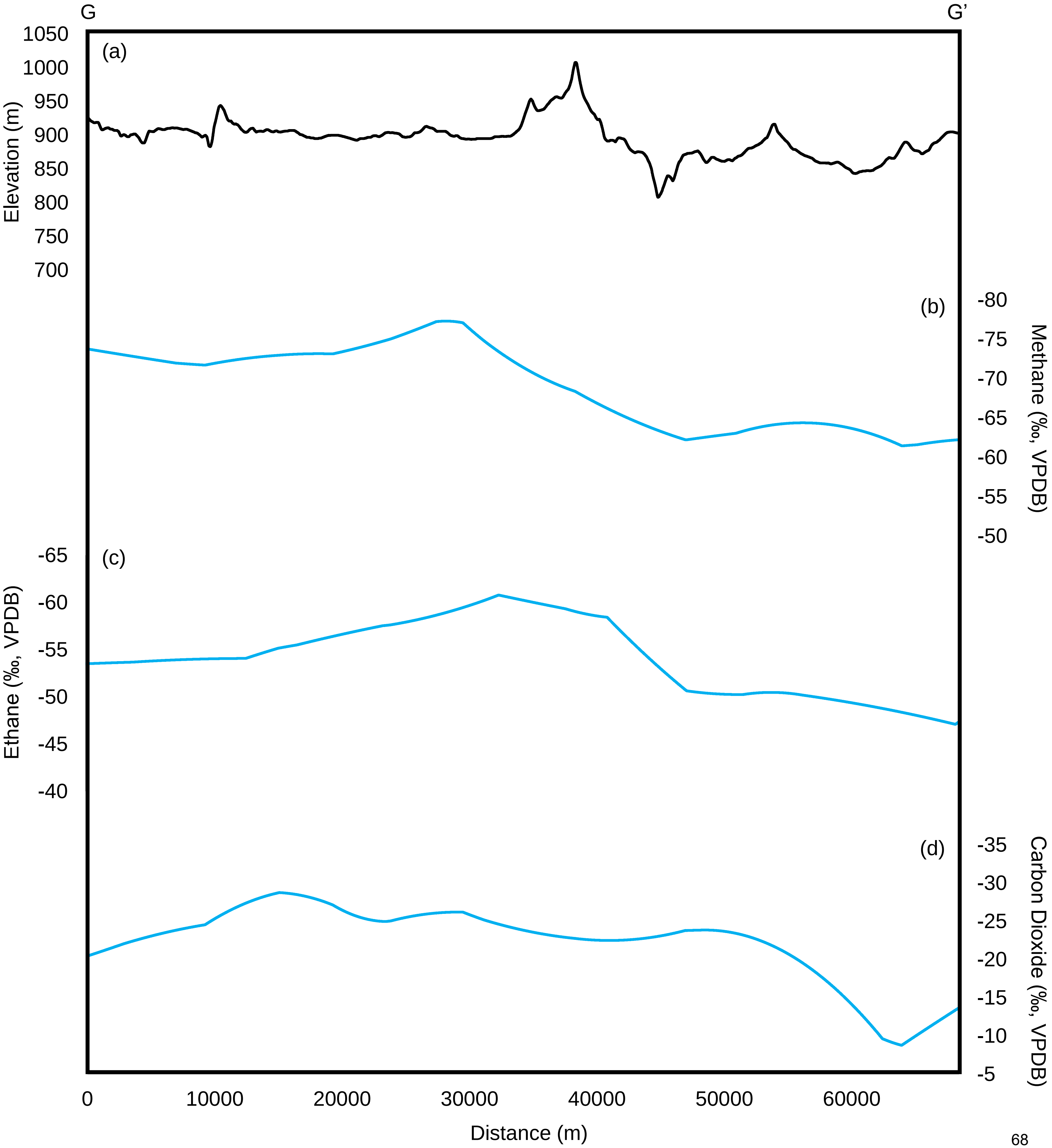


Fig. 42b. Topographic cross section (a), WW (b) and SCV (c) methane isotopic composition profiles from G to G'

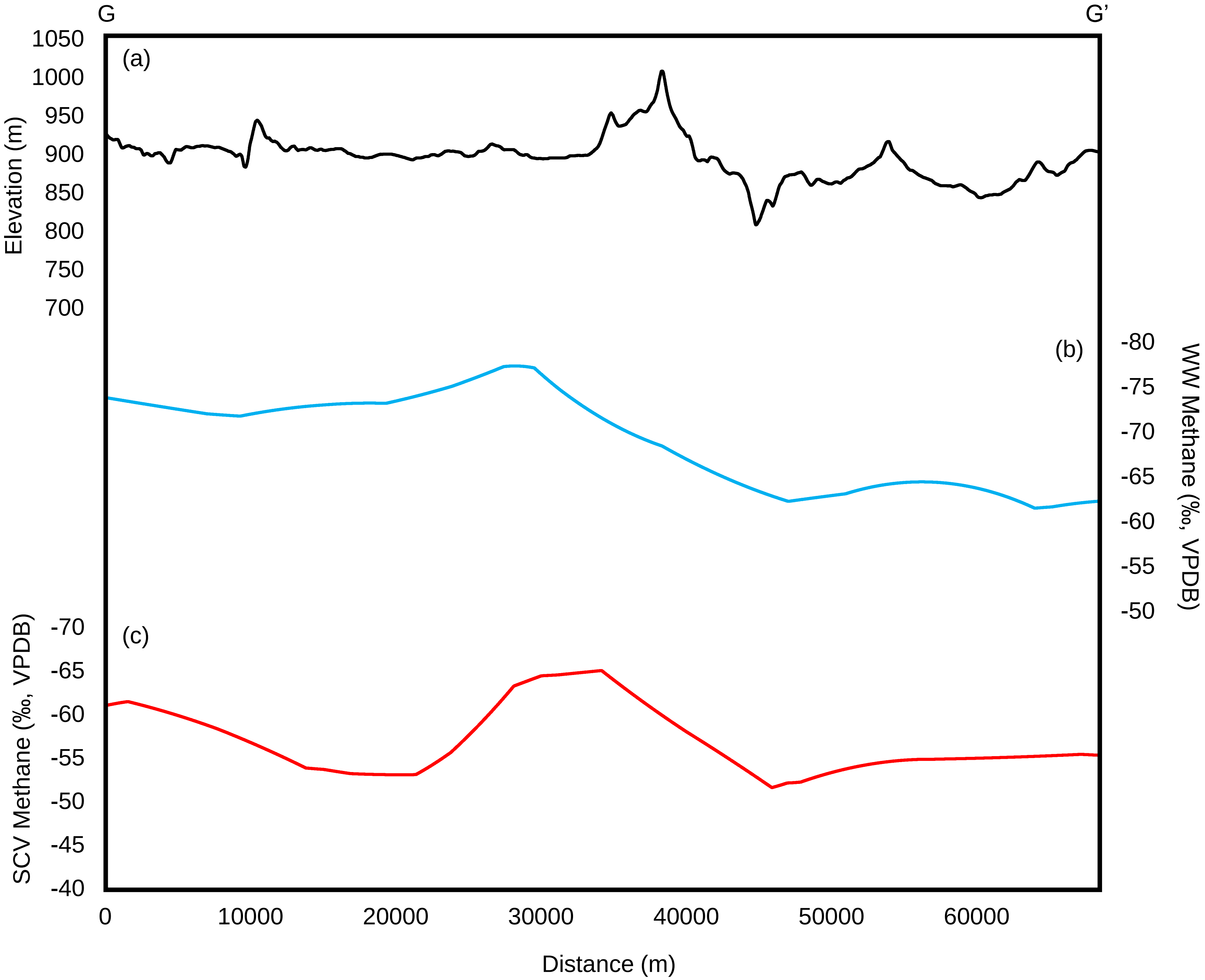


Fig. 42c. Topographic cross section (a), WW (b) and SCV (c) ethane isotopic composition profiles from G to G’

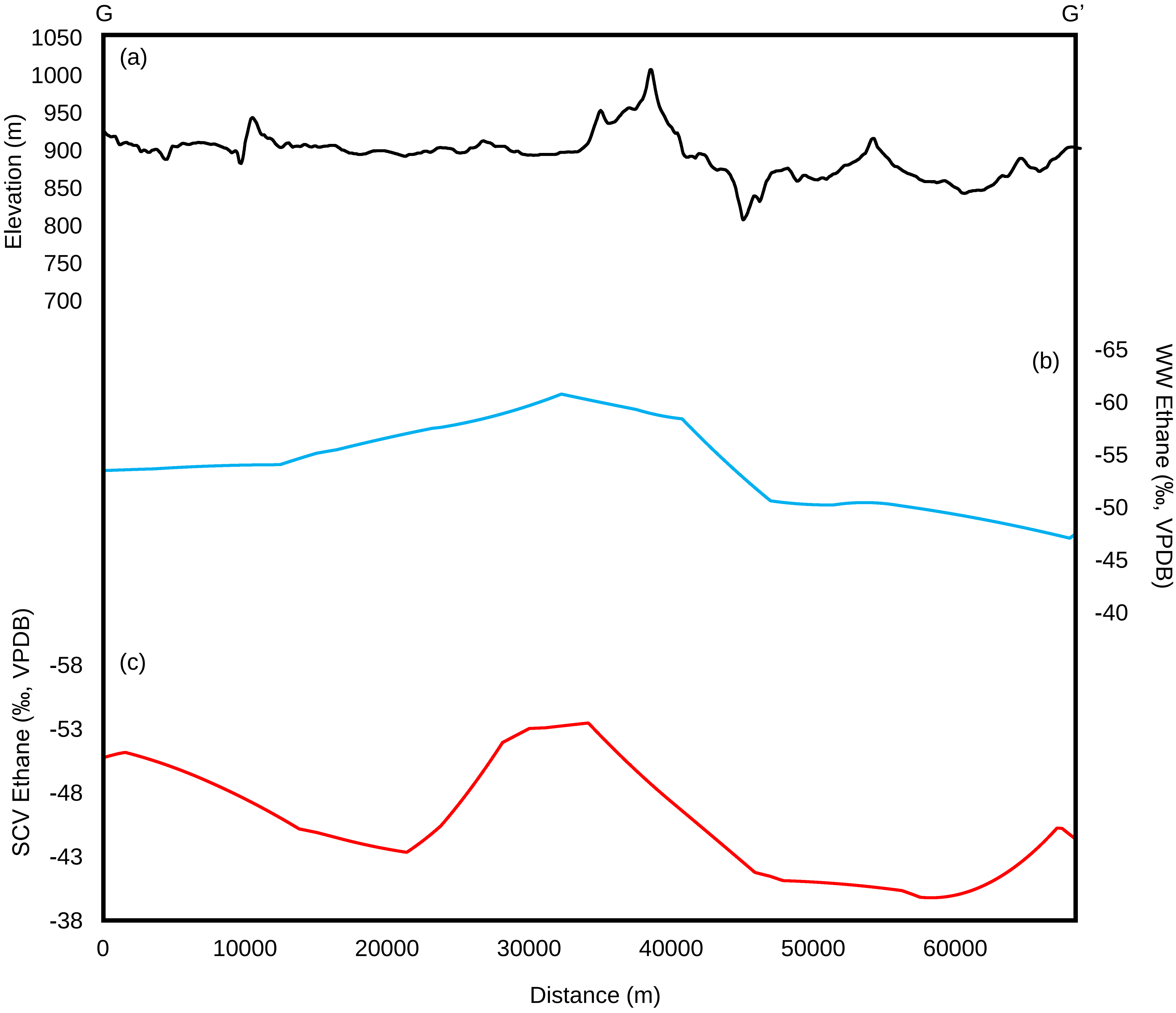


Fig. 42d. Topographic cross section (a), WW (b) and SCV (c) carbon dioxide isotopic composition profiles from G to G’

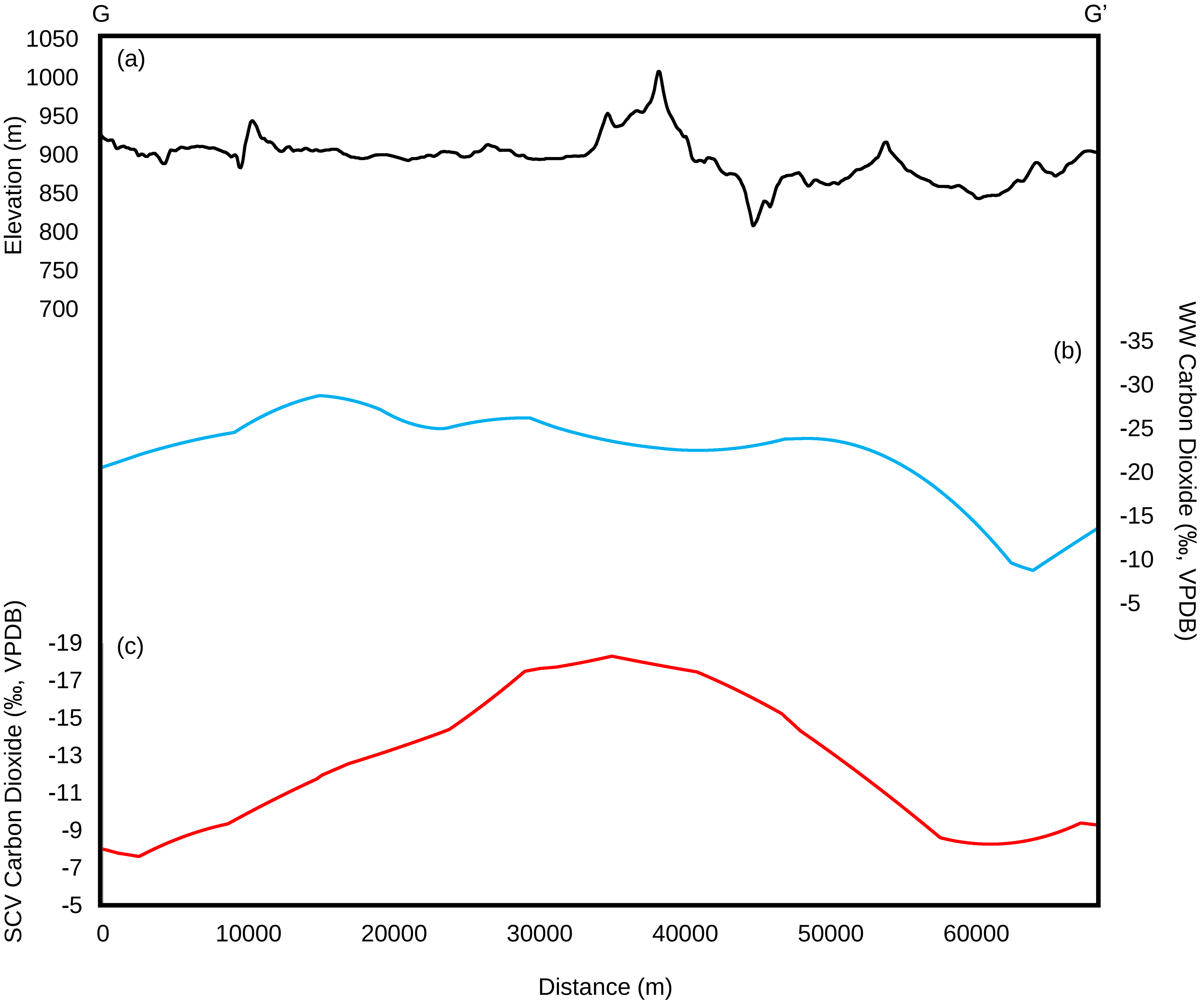


Fig. 43a. Topographic cross section (a), methane (b), ethane (c) and carbon dioxide (d) isotopic composition profiles from H to H’

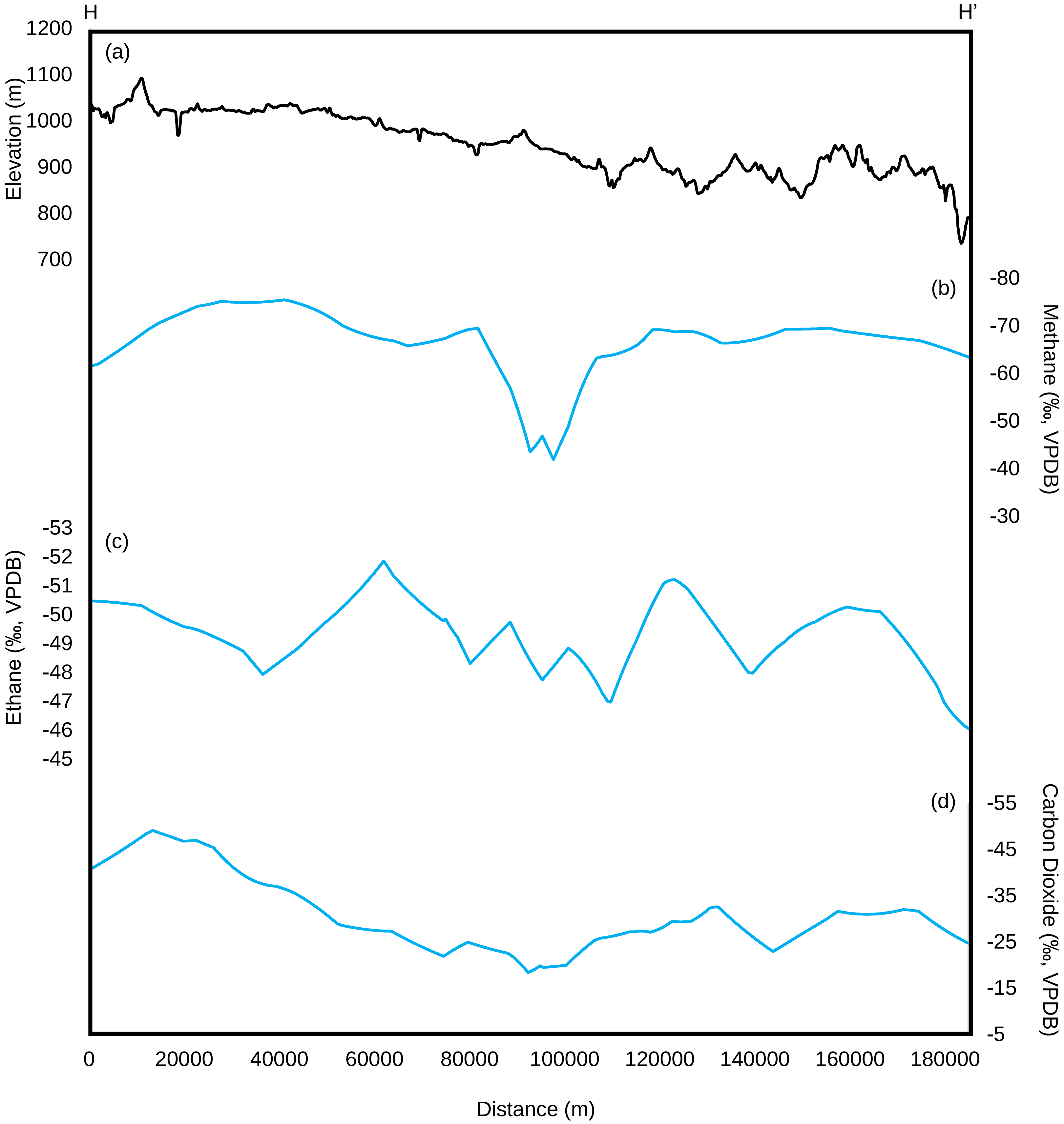


Fig. 43b. Topographic cross section (a), WW (b) and SCV (c) methane isotopic composition profiles from H to H’

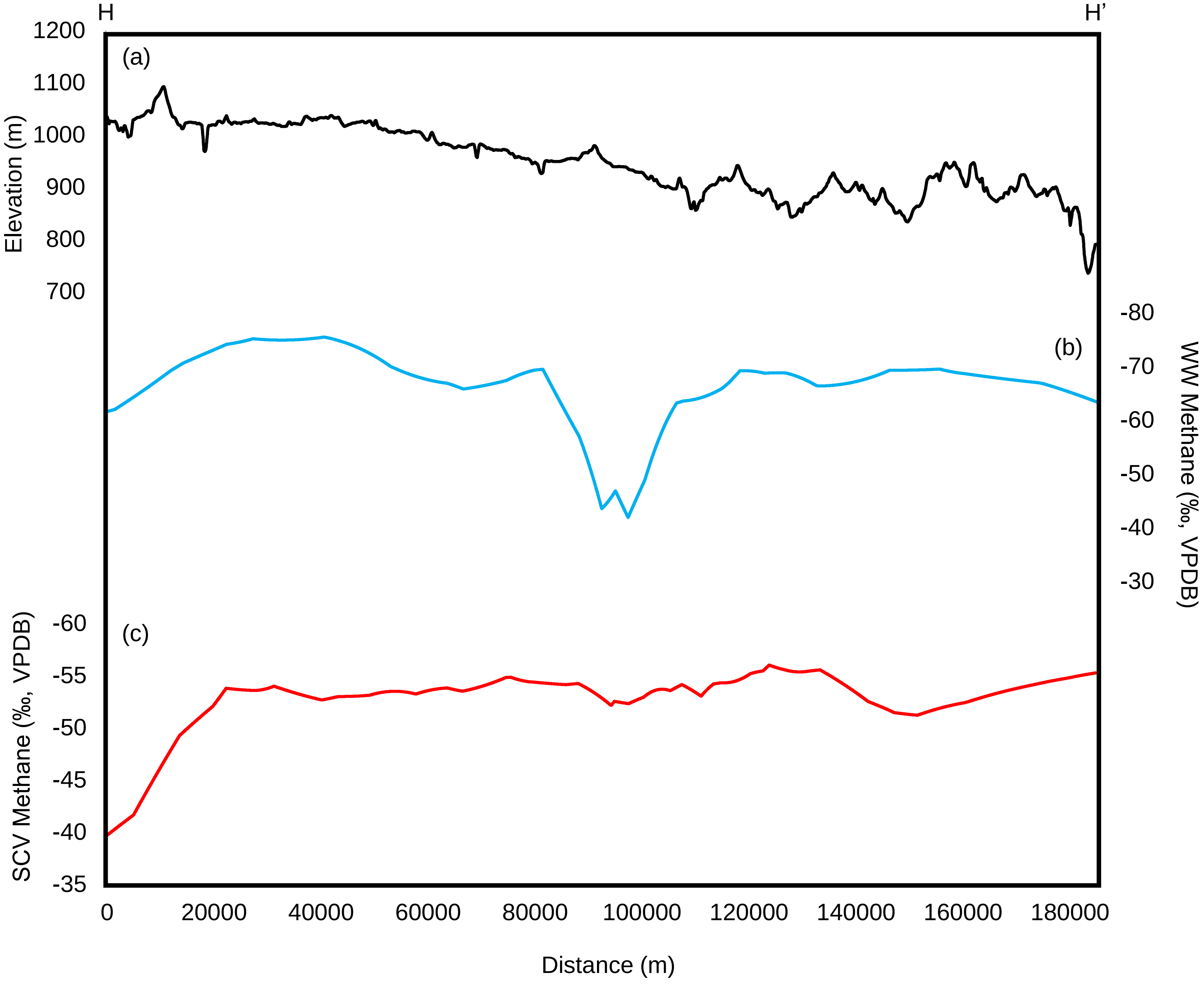


Fig. 43c. Topographic cross section (a), WW (b) and SCV (c) ethane isotopic composition profiles from H to H’

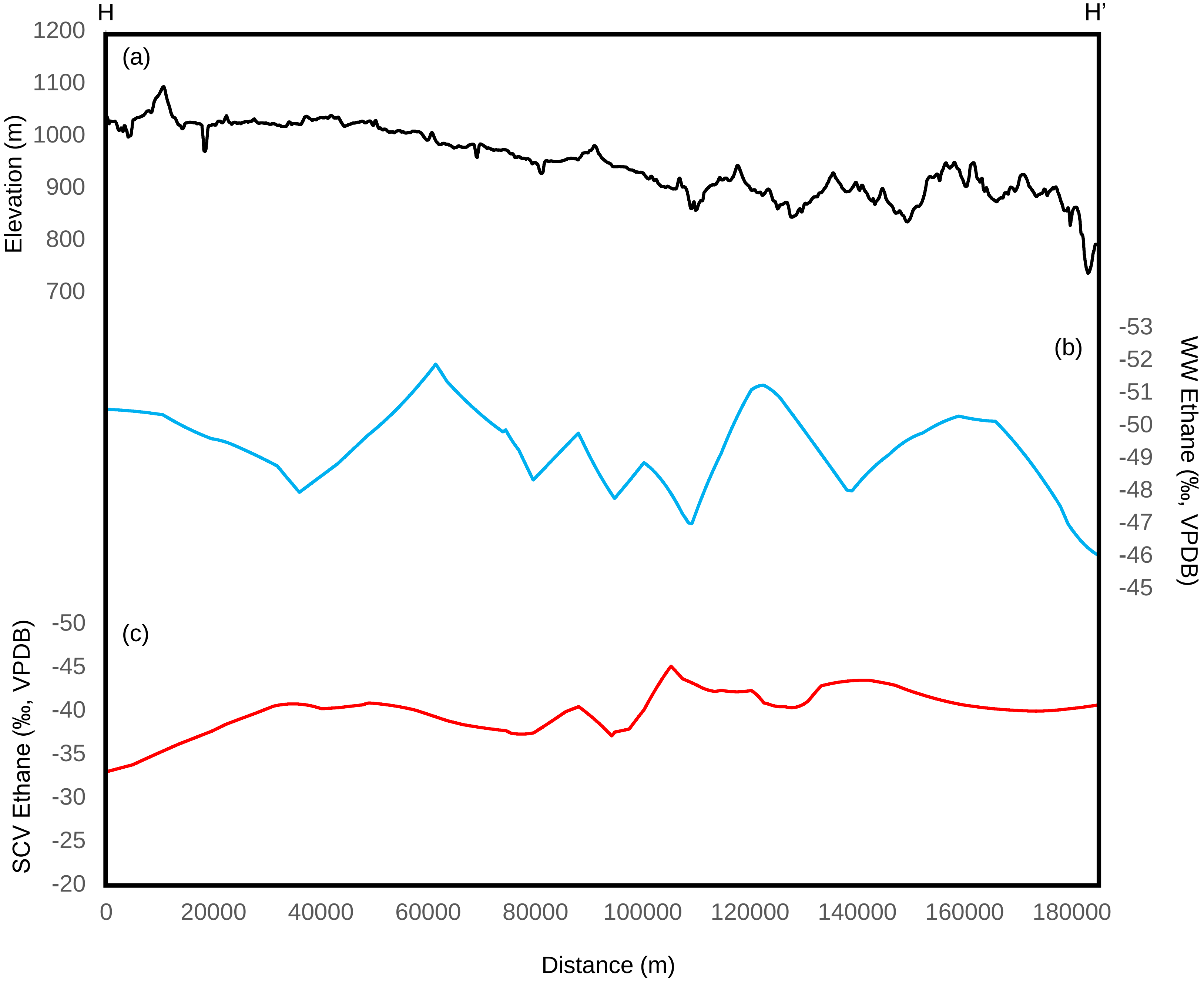


Fig. 44a. Topographic cross section (a), methane (b), ethane (c) and carbon dioxide (d) isotopic composition profiles from F to F’

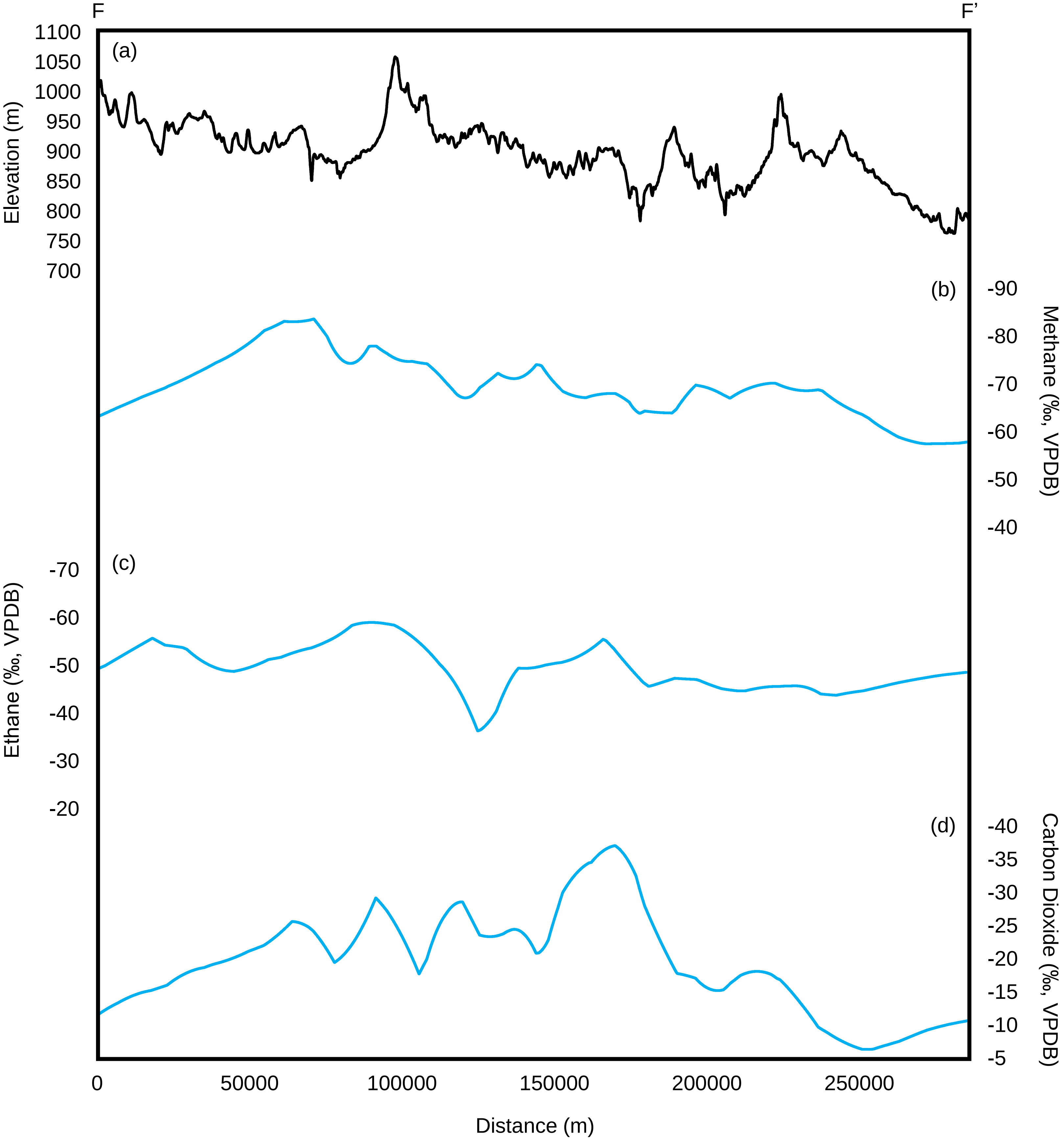


Fig. 44b. Topographic cross section (a), WW (b), GM (c), and SCV (d) methane isotopic composition profiles from F to F’

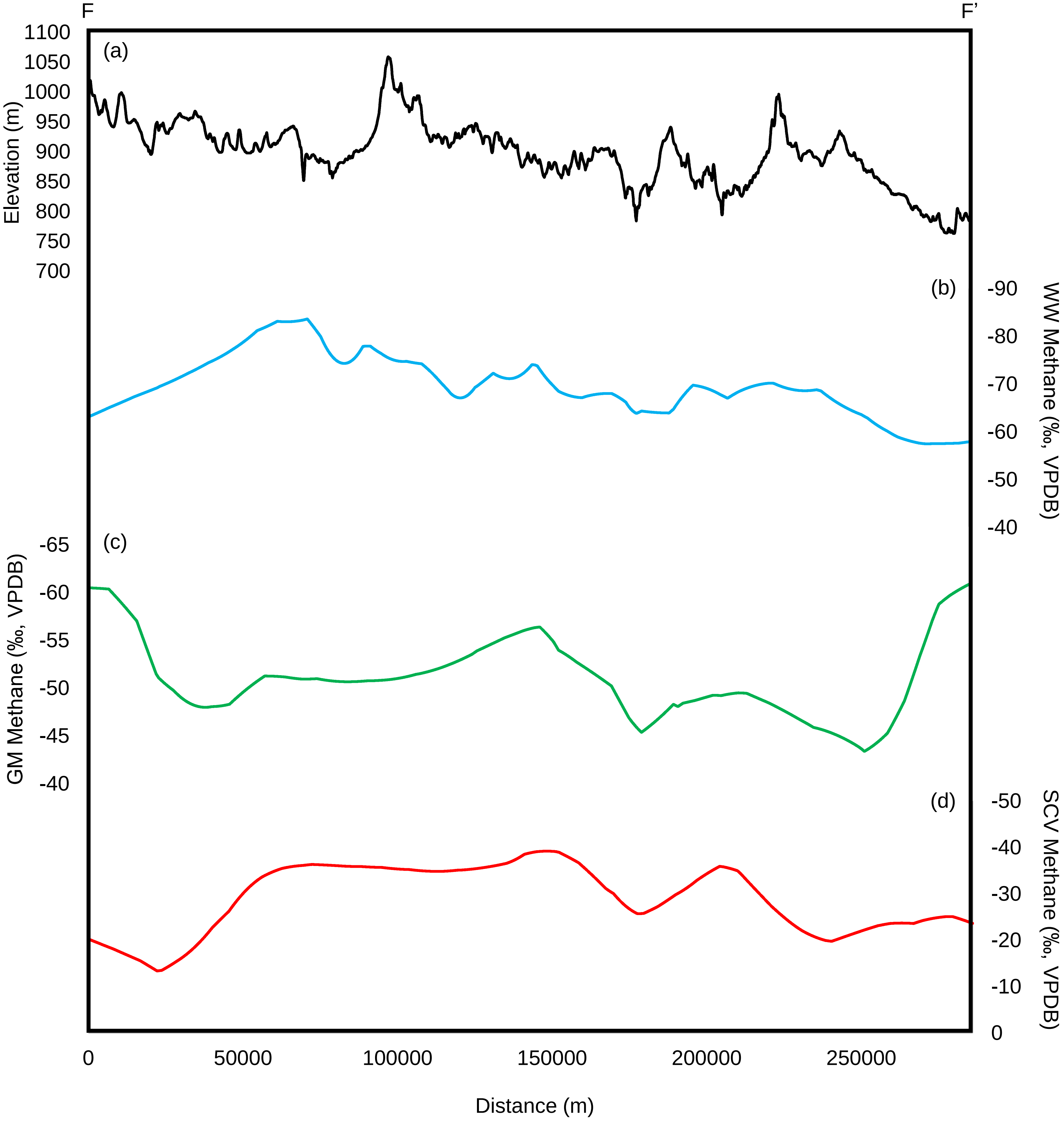


Fig. 44c. Topographic cross section (a), WW (b), GM (c), and SCV (d) ethane isotopic composition profiles from F to F’

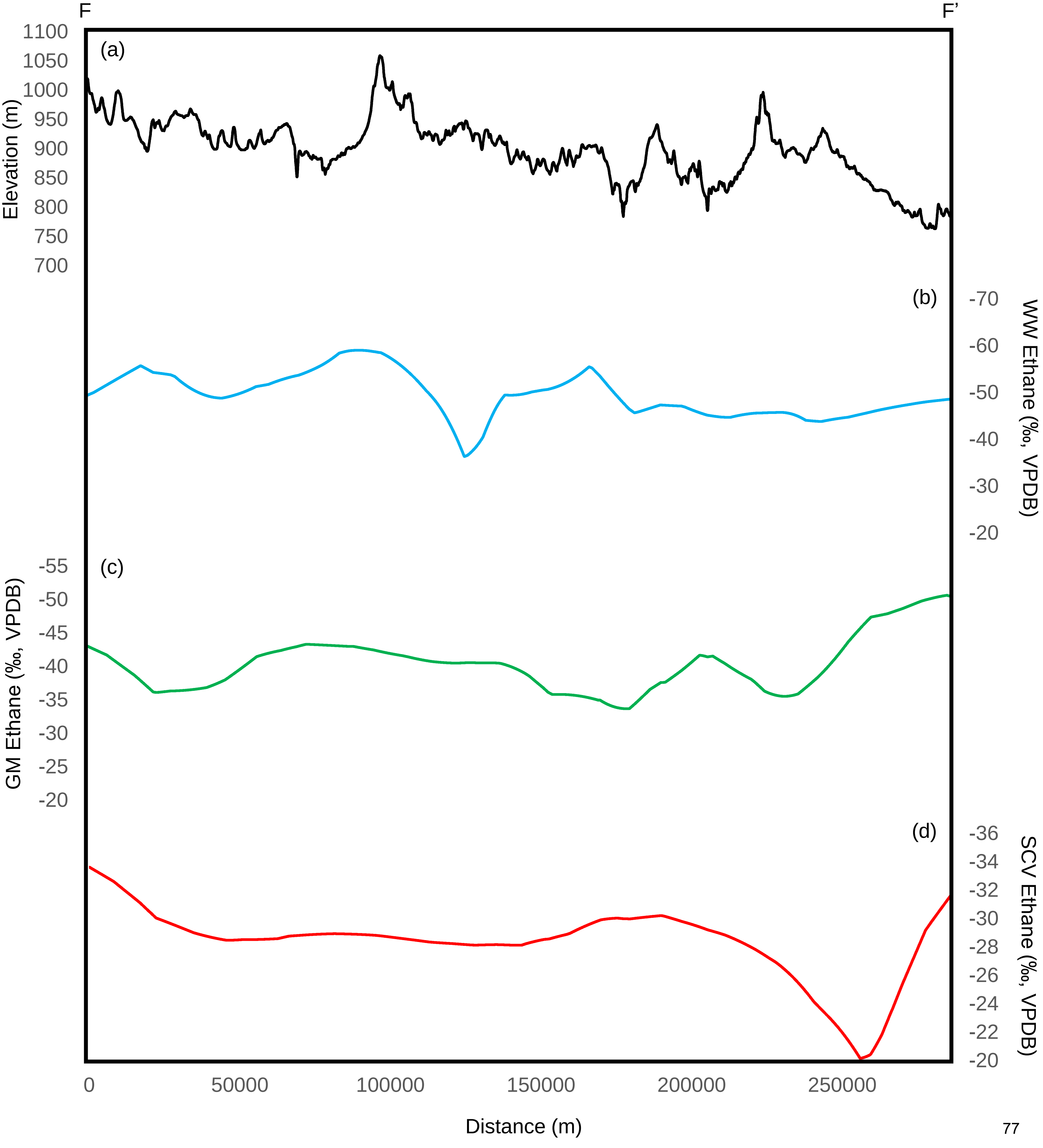


Fig. 44d. Topographic cross section and WW, GM and SCV carbon dioxide isotopic composition profiles from F to F’

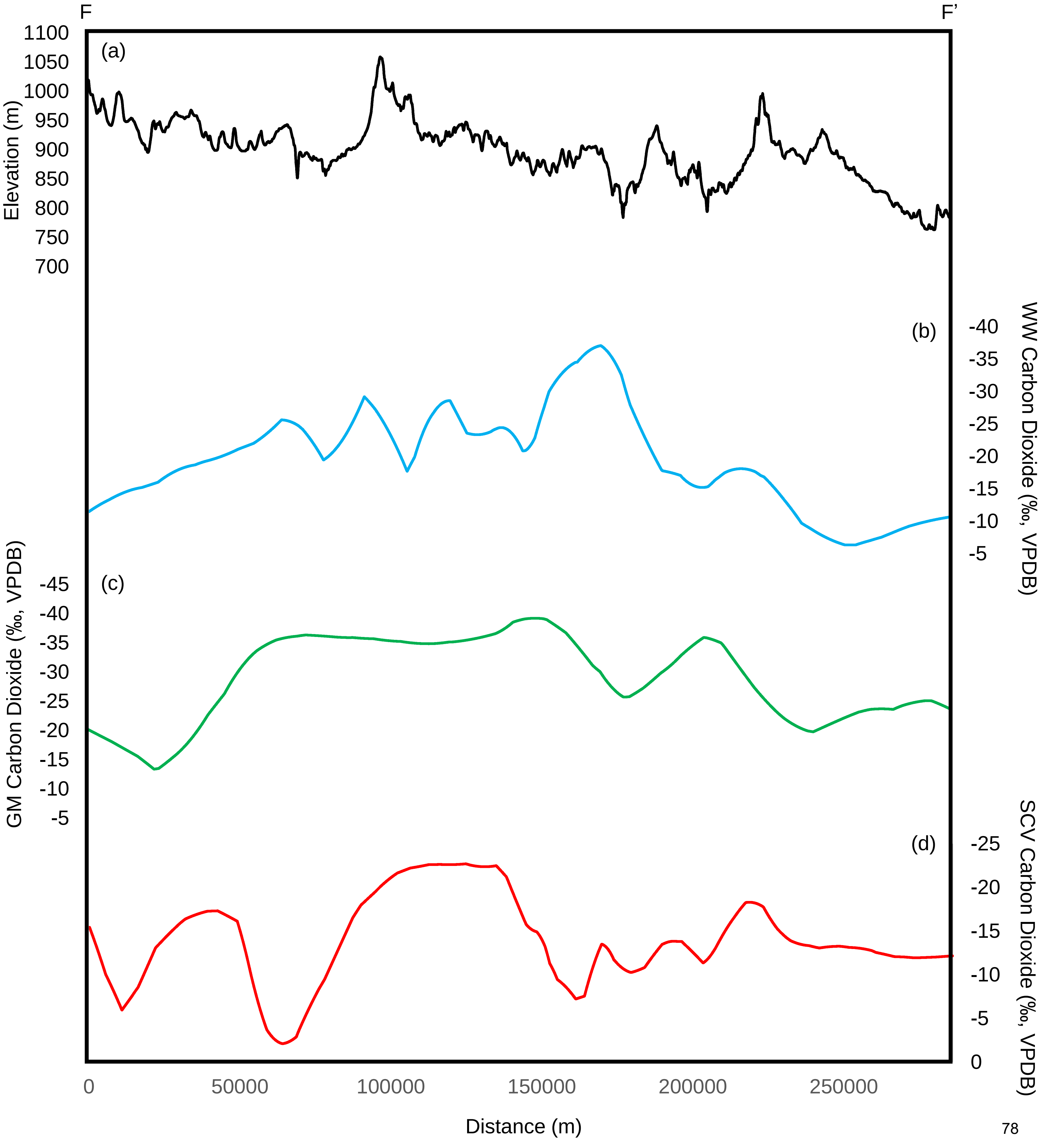


Fig. 45a. Topographic cross section and water well methane, ethane and carbon dioxide isotopic composition profiles from I to I’

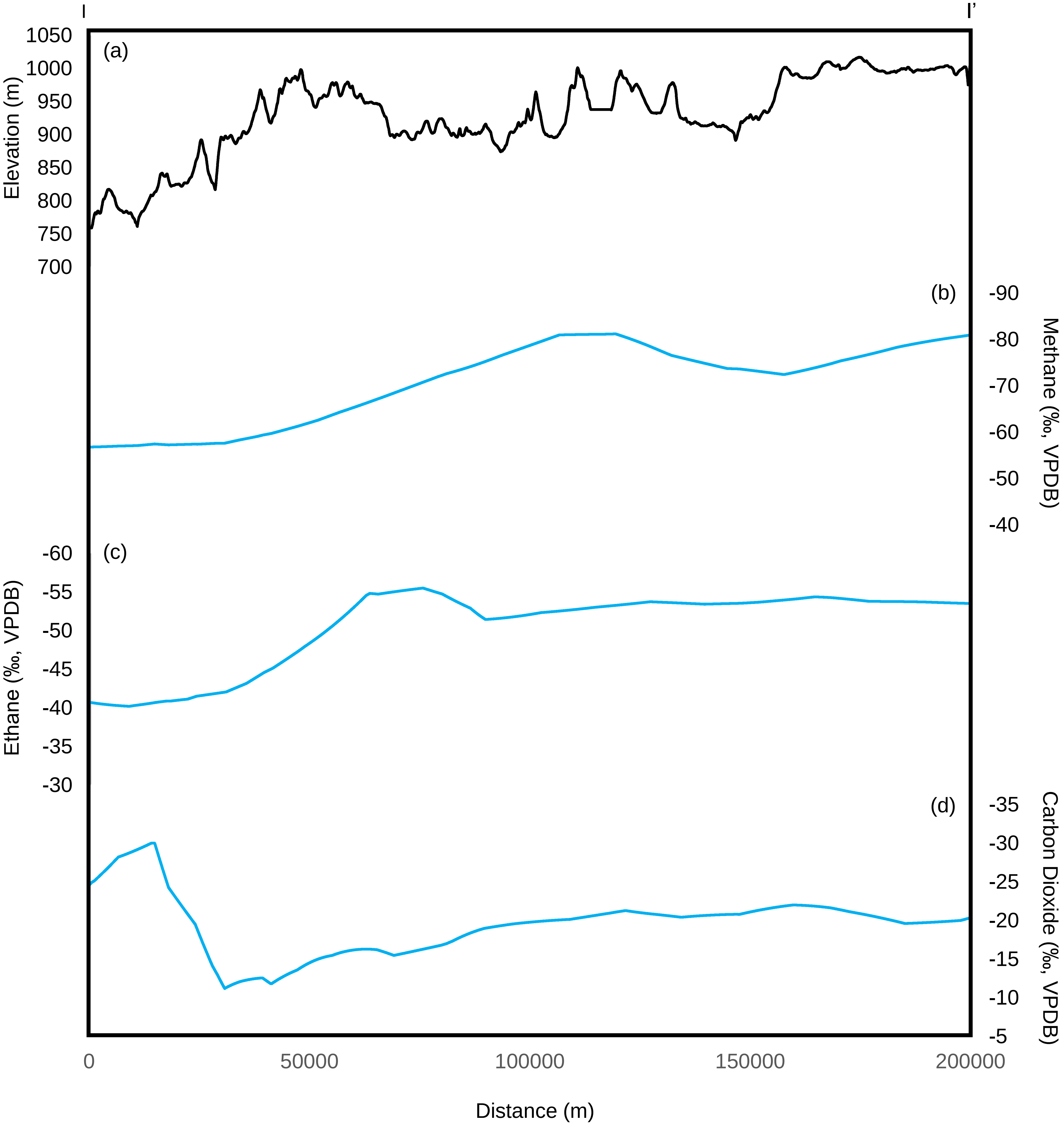


Fig. 45b. Topographic cross section and WW, GM and SCV methane isotopic composition profiles from I to I'

Fig. 45c. Topographic cross section and WW, GM and SCV ethane isotopic composition profiles from I to I’

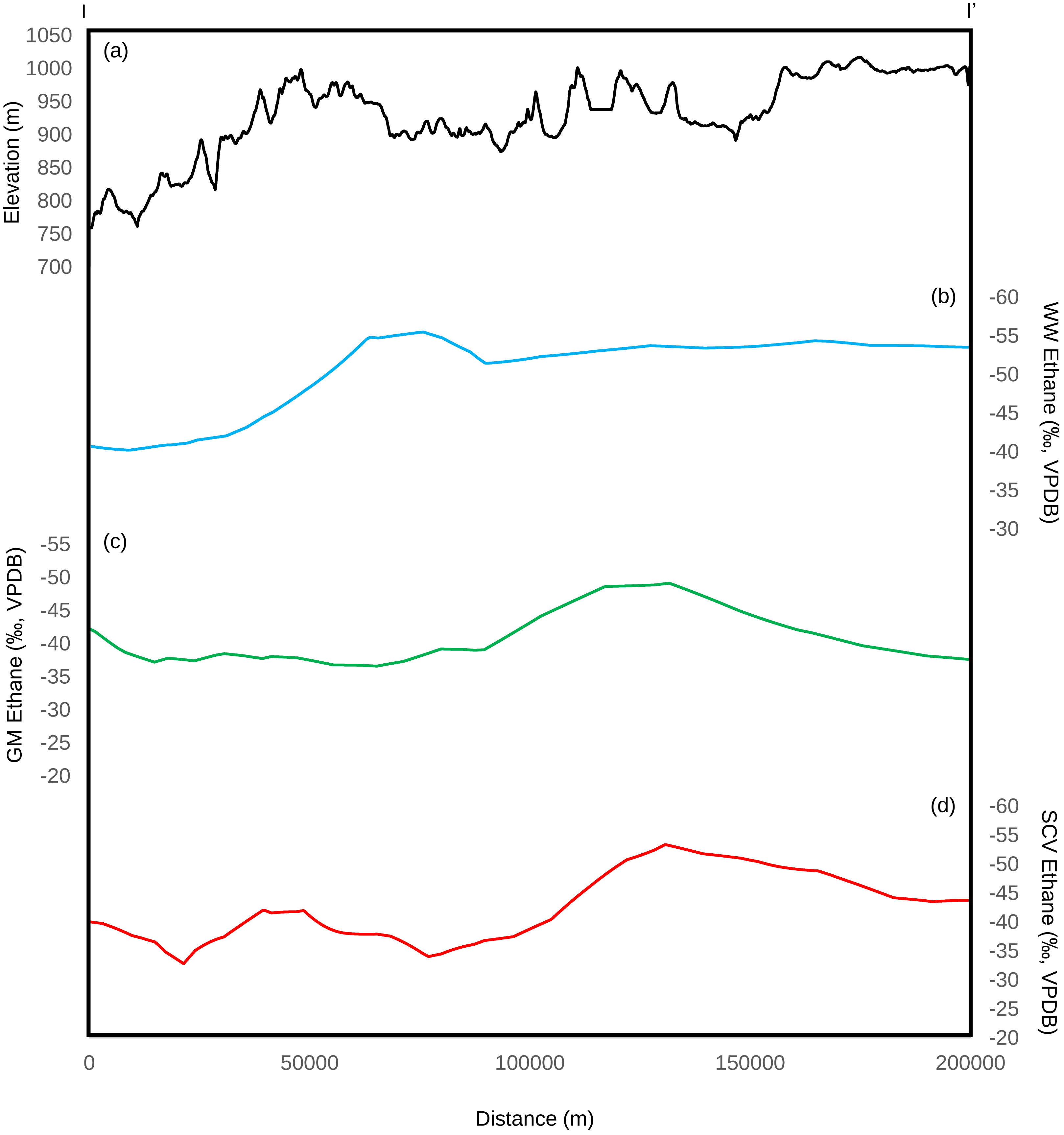


Fig. 45d. Topographic cross section and WW, GM and SCV carbon dioxide isotopic composition profiles from I to I’

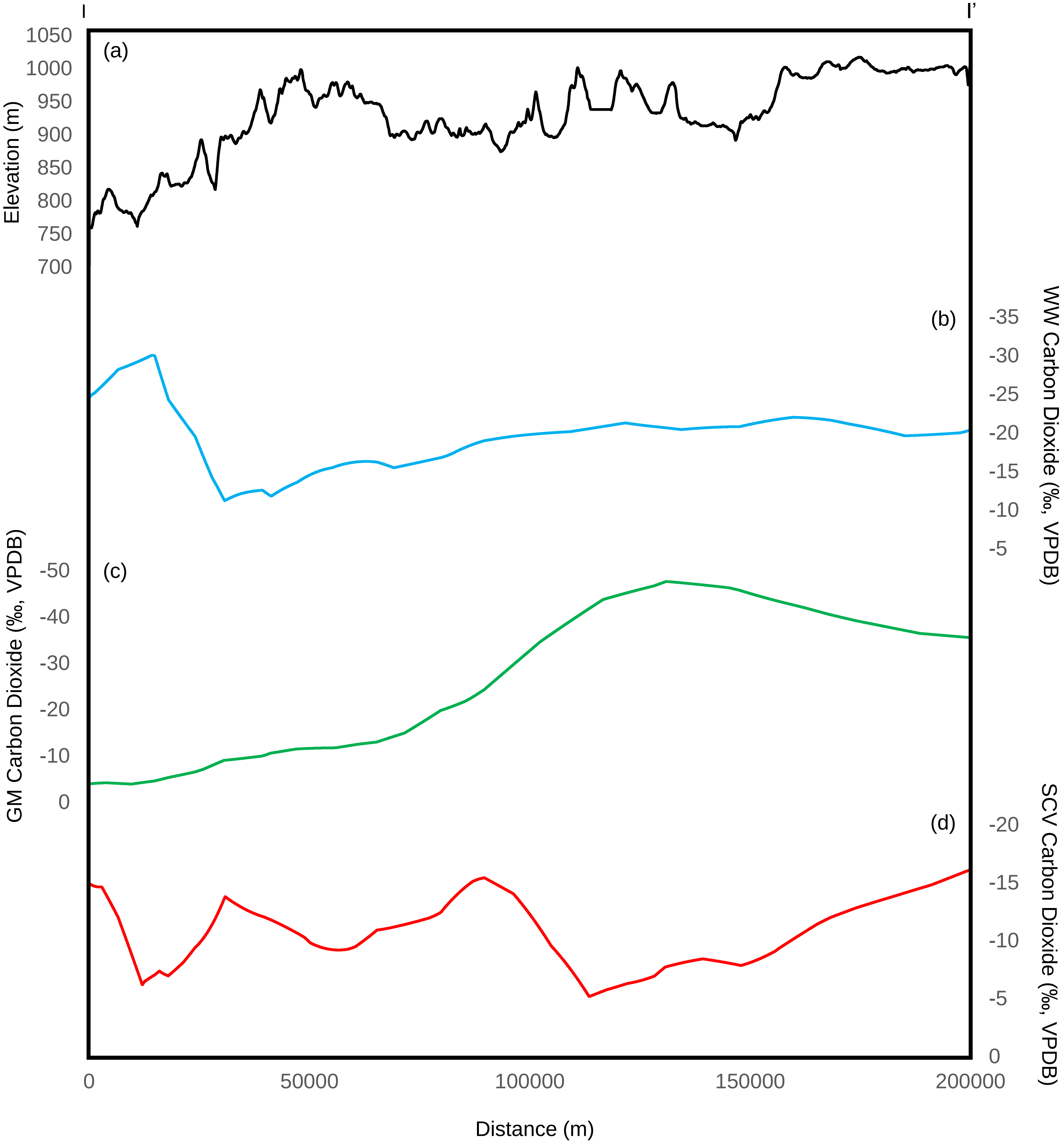


Fig. 46. Comparison of contour maps of methane carbon isotopic composition from domestic water wells (WW), ground migration (GM) and surface casing vent (SCV) in zoomed area

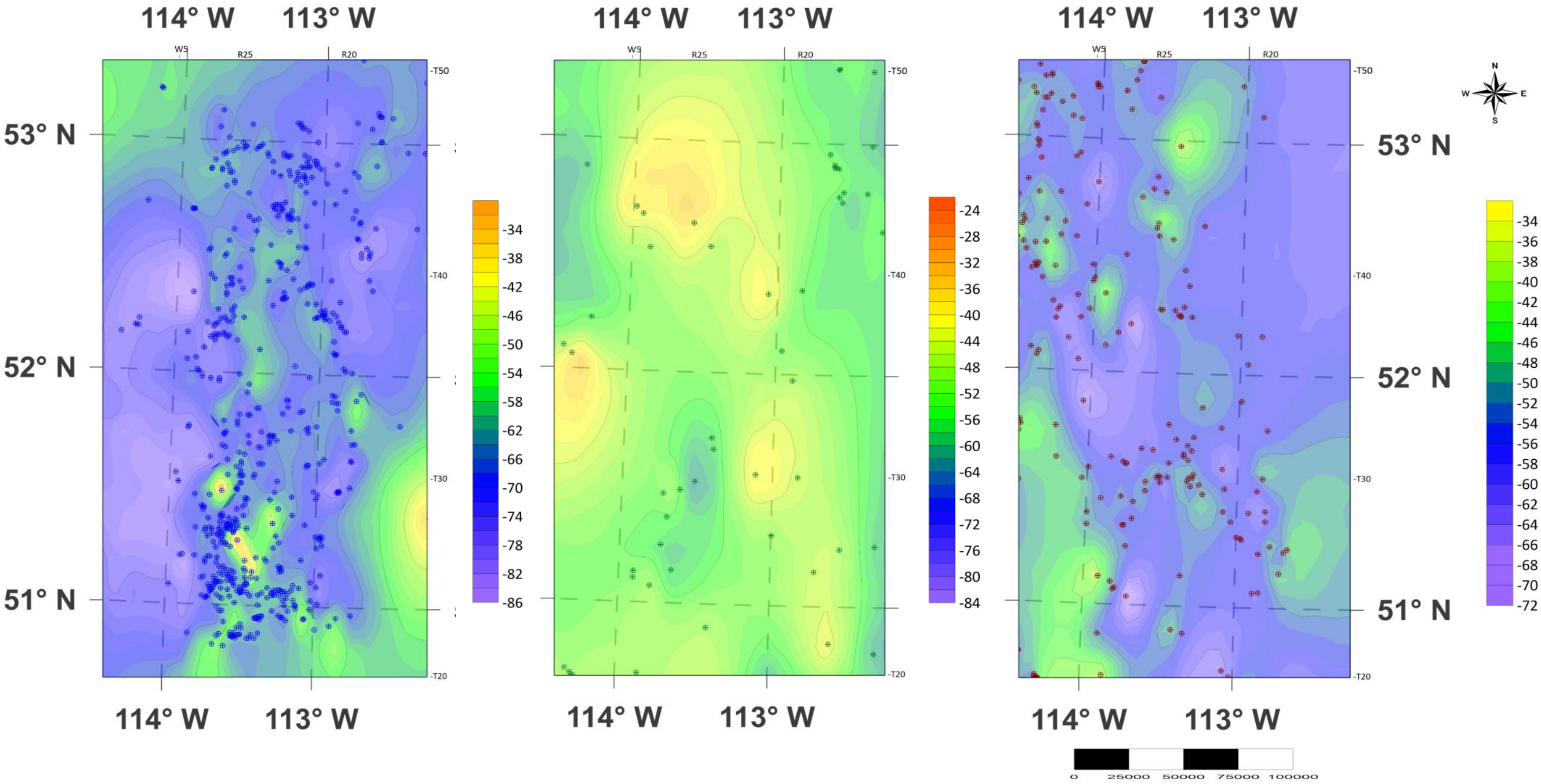
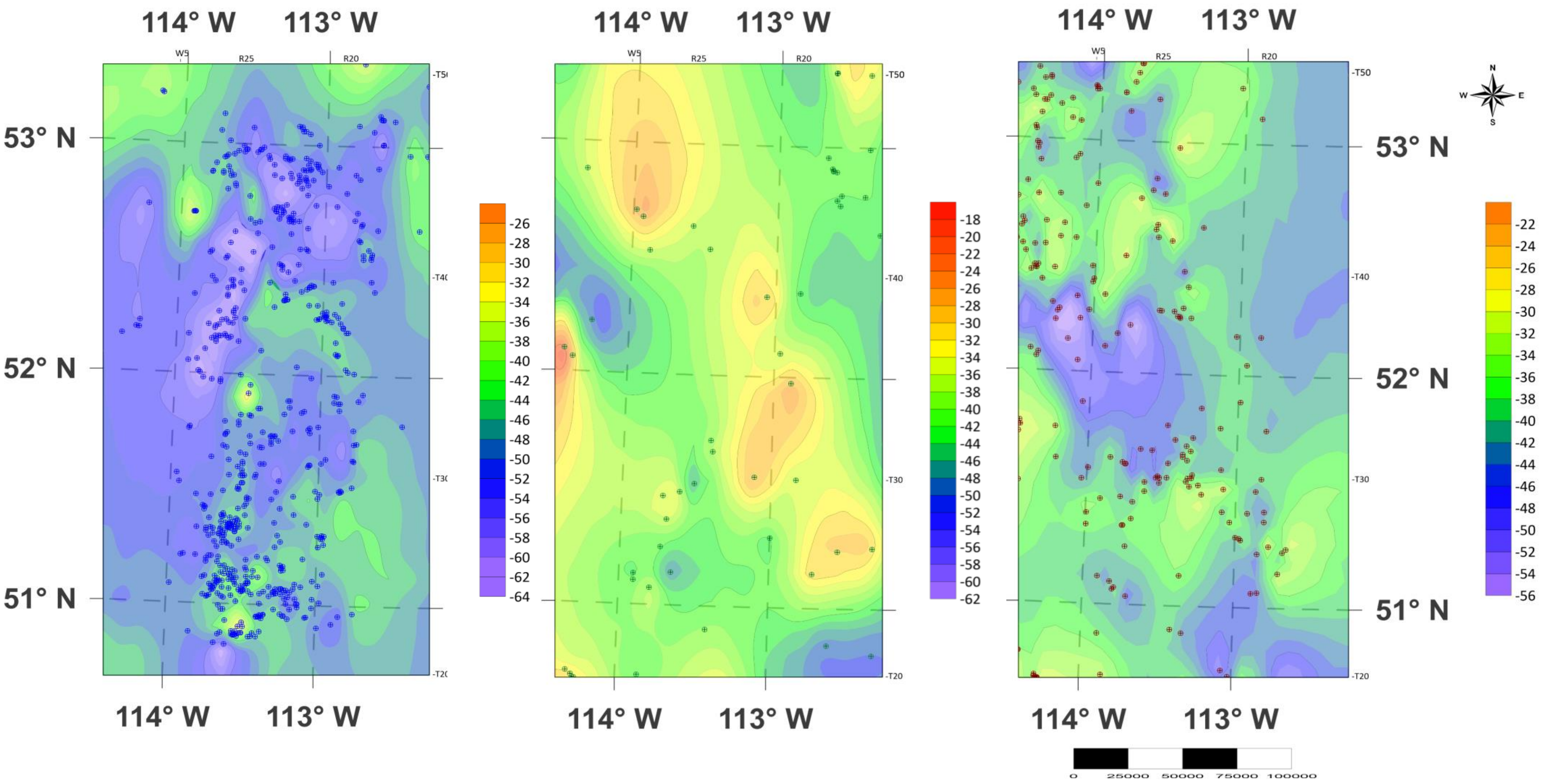

(a) Water Wells (b) Ground Migration (c) Surface Casing Vent

Fig. 47. Comparison of contour maps of ethane carbon isotopic composition from domestic water wells (WW), ground migration (GM) and surface casing vent (SCV) in zoomed area



(a) Water Wells

(b) Ground Migration

(c) Surface Casing Vent