Supplementary Material for:

**THERMOBAROMETRY OF THREE SKARNS IN THE LUDWIG AREA, NEVADA, BASED ON RAMAN SPECTROSCOPY AND ELASTIC MODELING OF MINERAL INCLUSIONS IN GARNET**

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Table A1. SAMPLE IDS, COORDINATES AND DESCRIPTIONS.

|  |  |  |
| --- | --- | --- |
| **Sample ID** | **Location**  **Lat (°N) Long (°W)** | **Sample Descriptions** |
| DH01 | 38°57’03.03” N 119°16’14.82” W | 3 quartz + 3 apatite inclusions at depth, 1 quartz inclusion at sample surface, pyroxene inclusions present in garnet core, suitable for standards and mineral inclusion analysis |
| DH02 | 38°57’02.01” N 119°16’13.61” W | 3 quartz + 4 apatite + 3 calcite inclusions at depth, several quartz inclusions near sample surface or cracks, 1 calcite inclusion at sample surface, sparse pyroxene inclusions present, suitable for standards and mineral inclusion analysis |
| DH03 | 38°57’02.01” N 119°16’13.61” W | 3 quartz + 5 apatite + 1 zircon inclusions at depth, contains epidote with quartz inclusions on outer surface of garnet and primary fluid inclusion assemblages, suitable for mineral inclusion analysis |
| DH04 | 38°57’02.65” N 119°16’14.90” W | 3 quartz + 3 apatite + 2 calcite inclusions at depth, 1 quartz + 1 calcite inclusion at sample surface, sparse pyroxene and fluid inclusions in garnet, no clear fluid inclusion assemblages, suitable for standards and mineral inclusion analysis |
| DH05 | 38°57’01.65” N 119°16’14.65” W | 4 quartz + 1 calcite inclusions at depth, no apatite inclusions present, 1 quartz inclusion at sample surface, pyroxene inclusions present, suitable for standards and mineral inclusion analysis |
| DH06 | 38°57’01.65” N 119°16’14.65” W | 3 quartz inclusions at depth, only one apatite inclusion located near surface, 1 quartz inclusion at sample surface, sparse fluid inclusions present, suitable for quartz inclusion analysis |
| MH01 | 38°57’06.58” N 119°16’10.45” W | 1 quartz + 3 apatite inclusions at depth, 1 quartz inclusion at sample surface, sparse fluid inclusions present, pyroxene, and 1 monticellite inclusion, suitable for standards and mineral inclusion analysis |
| MH03 | 38°57’06.58” N 119°16’10.45” W | 1 quartz + 1 calcite + 1 zircon inclusions at depth, many pyroxene inclusions towards core, sparse magnetite and monticellite inclusions present mostly in garnet cores, suitable for mineral inclusion analysis |
| MH04 | 38°57’06.58” N 119°16’10.45” W | 3 quartz + 2 apatite + 2 calcite inclusions at depth, 2 other apatite inclusions located near surface but not exposed, fluid inclusions present but no clear assemblages, suitable for mineral inclusion analysis |
| MH05 | 38°57’07.39” N 119°16’10.01” W | 1 quartz inclusion at depth, apatite inclusions located too close to surface or cracks, sparse fluid, pyroxene, and calcite inclusions present, suitable for mineral inclusion analysis |
| MH06 | 38°57’07.39” N 119°16’10.01” W | 2 quartz + 2 apatite inclusions at depth, 2 quartz + 1 apatite inclusions located at sample surface, suitable for standards and mineral inclusion analysis |
| MH08 | 38°57’10.44” N 119°16’10.37” W | 2 quartz + 3 apatite + 1 calcite inclusions at depth, sparse fluid inclusions and several pyroxene inclusions in garnet core present, suitable for mineral inclusion analysis |
| MH09 | 38°57’10.44” N 119°16’10.37” W | 2 quartz + 3 apatite inclusions at depth, one quartz inclusion located at sample surface, pyroxene and magnetite inclusions present with one pyroxene at sample surface, suitable for standard and mineral inclusion analysis |
| MH10 | 38°57’07.36” N 119°16’08.90” W | 1 quartz + 2 apatite inclusions at depth, sparse fluid inclusions present, 1 zircon and several pyroxene present near garnet core, suitable for mineral inclusion analysis |
| MH11 | 38°57’07.36” N 119°16’08.90” W | 3 quartz + 1 apatite inclusions at depth, 1 monticellite, and few pyroxene present in garnet core, suitable for mineral inclusion analysis |
| MH12 | 38°57’06.80” N 119°16’12.22” W | 2 quartz + 4 apatite + 1 calcite inclusions at depth, fluid inclusions present but no clear assemblages, pyroxene inclusions present, suitable for mineral inclusion analysis |
| MH13 | 38°57’06.80” N 119°16’12.22” W | 2 quartz inclusions at depth, no apatite inclusions at depth, pyroxene inclusions present mostly in garnet core, few towards rims, suitable for quartz inclusion analysis |
| CC01 | 38°56’ 44.70” N 119°16’24.50” W | Several apatite inclusions at depth, relict calcite grains present, suitable for mineral inclusion analysis |
| CC02 | 38°56’ 44.70” N 119°16’24.50” W | Abundant apatite + calcite inclusions at depth, apatite exposed at surface, suitable for standard and mineral inclusion analysis |
| CC03 | 38°56’ 44.60” N 119°16’23.20” W | Abundant apatite + calcite inclusions at depth, two apatites exposed at surface, prevalent zonations in garnet with apatite inclusions across them, large calcite grains present, sparse fluid inclusions, suitable for standard and mineral inclusion analysis |
| CC04 | 38°56’ 44.60” N 119°16’23.20” W | Few inclusions of apatite + hematite at depth, prevalent zonations in garnet, relict calcite grains, suitable for mineral inclusion analysis |
| CC05 | 38°56’ 44.60” N 119°16’23.20” W | Prevalent zonations, only one apatite inclusion present near crack, sparse fluid inclusions present, not suitable for mineral inclusion analysis |
| CC06 | 38°56’ 44.90” N 119°16’24.90” W | No apatite inclusions present, large calcite grains present, not suitable for mineral inclusion analysis |
| CC07 | 38°56’ 44.90” N 119°16’24.90” W | No apatite inclusions present, large calcite grains present, sparse fluid inclusions present, not suitable for mineral inclusion analysis |
| CC08 | 38°56’ 46.50” N 119°16’25.30” W | Abundant apatite inclusions at depth and two at the surface, several inclusions located near cracks, contains clusters of apatite inclusions and relict calcite grains, suitable for standard and mineral inclusion analysis |
| CC09 | 38°56’ 46.50” N 119°16’25.30” W | Few inclusions of apatite + hematite at depth, prevalent zonations in garnet, sparse fluid inclusions present, suitable for mineral inclusion analysis |
| CC10 | 38°56’ 44.40” N 119°16’25.50” W | Several apatite inclusions at depth, two located near cracks/ sample surface, large calcite grains present, suitable for mineral inclusion analysis |
| CC11 | 38°56’ 44.40” N 119°16’25.50” W | No apatite inclusions but contains both ilmenite and hematite inclusions, not suitable for mineral inclusion analysis |
| CC12 | 38°56’ 44.40” N 119°16’25.50” W | No apatite inclusions present, relict calcite grains and sparse magnetite and ilmenite inclusions, not suitable for mineral inclusion analysis |
| CC13 | 38°56’ 44.40” N 119°16’25.50” W | Two apatite inclusions, one located near surface, sparse fluid inclusions present but with no clear assemblages, not suitable for mineral inclusion analysis |
| CC14 | 38°56’ 45.20” N 119°16’25.50” W | Several apatite, hematite, and magnetite inclusions at depth, prevalent zonations, suitable for mineral inclusion analysis |
| CC15 | 38°56’ 45.20” N 119°16’25.50” W | No apatite inclusions present, ilmenite and magnetite inclusions present in garnet cores, not suitable for mineral inclusion analysis |
| CC16 | 38°56’ 45.20” N 119°16’25.50” W | Several apatite + calcite inclusions at depth, apatite located near cracks/ sample surface, sparse hematite and fluid inclusions present, suitable for mineral inclusion analysis |

TABLE A2.CAMECA SX100 MICROPROBE PETROSILICATE ANALYTICAL ROUTINE USED FOR MEASURING MAJOR, MINOR, AND TRACE ELEMENTS IN GARNET.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element** | **Routine** | **Spectrometer/ Crystal Arrangement** | **Beam Current** | **Measured X-ray Line** | **Standard** | **On-peak Counting Time (s)** | **Nominal Peak Position (10000\*sinθ units)** | **Positions of the (-) and (+) Backgrounds Relative to Main Peak Position (10000\*sinθ units)** | **Calculated Detection Limits (3σ; ppm)** |
| Na | sp1 | TAP | 20nA | Kα | Albite | 10 | 46258 | -600 +600 | 342 |

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Al | sp1 | TAP | 20nA | Kα | Anorthite | 10 | 32393 | -550 +550 | 294 |
| Ca | sp2 | LPET | 20nA | Kα | Anorthite | 10 | 38382 | -800 +600 | 144 |
| Ba | sp2 | LPET | 20nA | Lα | Barite | 10 | 31726 | -900 +400 | 454 |
| K | sp3 | LPET | 20nA | Kα | Orthoclase | 10 | 42762 | -500 +750 | 161 |
| Ti | sp3 | LPET | 20nA | Kα | Rutile | 10 | 31413 | -500 +1100 | 166 |
| Mg | sp4 | TAP | 20nA | Kα | Forsterite | 10 | 38416 | -525 +525 | 359 |
| Si | sp4 | TAP | 20nA | Kα | Orthoclase | 10 | 27678 | -670 +600 | 262 |
| Mn | sp5 | LLIF | 20nA | Kα | Rhodonite | 10 | 52199 | -900 +500 | 384 |
| Fe | sp5 | LLIF | 20nA | Kα | Fayalite | 10 | 48082 | -380 +850 | 434 |
| F | sp1 | TAP | 299nA | Kα | Sellaite | 20 | 71157 | -1500 +1200 | 606 |
| Y | sp1 | TAP | 299nA | Lα | YAG | 100 | 25049 | -275 +200 | 73 |
| Ga | sp1 | TAP | 299nA | Lα | GGG | 100 | 43865 | -620 +620 | 108 |
| Cl | sp2 | LPET | 299nA | Kα | Marialite | 10 | 54033 | -425 +700 | 32 |
| Sr | sp2 | LPET | 299nA | Lα | SrTiO3 | 30 | 78433 | -2450 +1075 | 123 |
| P | sp2 | LPET | 299nA | Kα | Apatite | 40 | 70367 | -900 +930 | 33 |
| Sn | sp2 | LPET | 299nA | Lα | Cassiterite | 40 | 41143 | -800 +675 | 61 |
| V | sp3 | LPET | 299nA | Kα | V metal | 40 | 28613 | -800 +1100 | 28 |
| Cr | sp3 | LPET | 299nA | Kα | Chromite | 40 | 26169 | -800 +600 | 22 |
| Sc | sp3 | LPET | 299nA | Kα | Sc-diopside | 40 | 34640 | -550 +1730 | 22 |
| S | sp3 | LPET | 299nA | Kα | Barite | 40 | 61399 | -1900 +1550 | 33 |
| Zn | sp4 | TAP | 299nA | Lα | Zincite | 20 | 47602 | -3200 +1075 | 99 |
| Zr | sp4 | TAP | 299nA | Lα | Zircon | 100 | 23580 | -500 +700 | 122 |
| Ni | sp5 | LLIF | 299nA | Kα | Ni-diopside | 40 | 41175 | -500 +700 | 51 |
| Co | sp5 | LLIF | 299nA | Kα | Co-diopside | 40 | 44429 | -400 +500 | 46 |
| Cu | sp5 | LLIF | 299nA | Kα | Chalcopyrite | 10 | 38260 | -500 +500 | 150 |

\*For further details, see <https://www.rockptx.com/wp-content/uploads/2017/02/microprobe-analytical-routines-2016.pdf>

\*\*All analyses were taken at 20 kV

Table A3. CAMECA SX100 MICROPROBE PETROAPATITE ANALYTICAL ROUTINE USED FOR MEASURING MAJOR, MINOR, AND TRACE ELEMENTS IN APATITE.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Element** | **Routine** | **Spectrometer/ Crystal Arrangement** | **Beam Current** | **Measured X-ray Line** | **Standard** | **On-peak Counting Time (s)** | **Nominal Peak Position (10000\*sinθ units)** | **Positions of the (-) and (+) Backgrounds Relative to Main Peak Position (10000\*sinθ units)** | **Calculated Detection Limits (3σ; ppm)** |
| F | sp1 | TAP | 20nA | Kα | Apatite | 20 | 71157 | -1500 +1500 | 1346 |
| Na | sp1 | TAP | 20nA | Kα | Albite | 10 | 46258 | -600 +600 | 407 |
| Ca | sp2 | LPET | 20nA | Kα | Apatite | 10 | 38382 | -800 +600 | 214 |
| Cl | sp2 | LPET | 20nA | Kα | Marialite | 10 | 54033 | -425 +700 | 100 |
| P | sp3 | LPET | 20nA | Kα | Apatite | 10 | 70367 | -900 +930 | 303 |
| Mn | sp5 | LLIF | 20nA | Kα | Rhodonite | 10 | 52199 | -900 +500 | 481 |
| Fe | sp5 | LLIF | 20nA | Kα | Fayalite | 10 | 48082 | -380 +850 | 585 |
| Y | sp1 | TAP | 299nA | Lα | YAG | 60 | 25049 | -275 +200 | 62 |
| As | sp1 | TAP | 299nA | Lα | NiAs | 60 | 37565 | -850 +1800 | 32 |
| Th | sp2 | LPET | 299nA | Mα | Thorianite | 50 | 47294 | -500 +500 | 127 |
| U | sp2 | LPET | 299nA | Mβ | Uraninite | 50 | 42466 | -625 +450 | 156 |
| Sr | sp2 | LPET | 299nA | Lα | SrTiO3 | 20 | 78433 | -2450 +1075 | 139 |
| V | sp3 | LPET | 299nA | Kα | V metal | 90 | 28613 | -800 +1100 | 29 |
| S | sp3 | LPET | 299nA | Lα | Barite | 30 | 61399 | -1900 +1550 | 29 |
| Si | sp4 | TAP | 299nA | Kα | Orthoclase | 10 | 27678 | -670 +600 | 200 |
| As | sp4 | TAP | 299nA | Lα | NiAs | 110 | 37565 | -850 +1800 | 32 |
| La | sp5 | LLIF | 299nA | Lα | REE3 glass | 20 | 66202 | -855 +600 | 229 |
| Ce | sp5 | LLIF | 299nA | Lβ | REE3 glass | 20 | 58526 | -340 +975 | 493 |
| Pr | sp5 | LLIF | 299nA | Lβ | REE3 glass | 20 | 56090 | -700 +240 | 420 |
| Nd | sp5 | LLIF | 299nA | Lβ | REE2 glass | 20 | 53812 | -600 +420 | 453 |
| Sm | sp5 | LLIF | 299nA | Lβ | REE2 glass | 20 | 49622 | -300 +345 | 465 |
| Gd | sp5 | LLIF | 299nA | Lβ | REE1 glass | 20 | 45867 | -300 +300 | 471 |

\*For further details, see <https://www.rockptx.com/wp-content/uploads/2017/02/microprobe-analytical-routines-2016.pdf>

\*\*20 kV accelerating voltage used for all analysis condition

*H2O Substitution in Garnet*

There is a possibility for H2O to substitute into the structure of garnet in the form of the 4H for 1Si exchange in the T crystallographic site. This may be particularly true for skarn garnets as they are formed by an aqueous fluid. This substitution may be present in these garnet samples as the Σcation values are <8 and there are slight charge imbalances and Si deficiencies encountered during garnet normalization in the absence of an assumed H2O content. In an attempt to account for these imbalances and deficiencies, we have estimated the average H2O content of the garnet from all three deposits to be ~0.18 wt. % by estimating an H2O content, calculating resultant T vacancies, then including the vacancies as an additional “cation” in the normalization. The values reported in the data tables do not account for this as it is an estimation and these values were not measured directly. If indeed present, this is a relatively small proportion of H2O and is unlikely to significantly affect the elastic parameters of the garnet and thus likely does not affect the results of this study to a significant degree.

*CO2 Substitution in Apatite*

It is also possible that CO2 could be present in apatite in the form of the CO3 for PO4 exchange in the T crystallographic site of apatite. This substitution may explain some of the charge imbalances which were encountered during apatite normalization, but this could also be due to the fact that these apatite grains were very small (~30 μm) and thus may be subject to some analytical contamination from the adjacent garnet which would affect the measured quantities of Si and Fe in these apatites (both appeared anomalously high). We have estimated the average CO2 content of the apatite from all three deposits to be ~0.45 wt. % by the same process as for H2O substitution in garnet: by estimating a possibly CO2 content, calculating the resultant T vacancies, then including the vacancies as an additional “cation” in the normalization. If accounted for, the presence of CO2 improves the charge balances and cation totals. However, the presences of CO2 substitution is essentially speculative, thus we have not included any correction for this in the data tables as CO2 content was not measured directly. As in the case of H2O substitution in garnet, if these small proportions of CO2 are indeed present, it would be unlikely to significantly affect the elastic parameters of the apatite and thus likely does not affect the results of this study to a significant degree.

*Equations for calculating inclusion pressure based on Raman shifts*

Inclusion *P’s* for fluorapatite inclusions at room *T* were determined using the *P*-sensitive frequency shift of the ca. 964 cm-1 band according to the following polynomial equation from Ashley et al. (2017), based on experimental data of Schouwink et al. (2010):

*P* (bar) = (*a* (Δ*ν964*)2*P,Tref*) + (*b* (Δ*ν964*)*P,Tref*)

where *a* and *b* are regression parameters equal to 7.35 ± 1.88 and 2265 ± 59, respectively. The parameter (Δ*ν964*)*P,Tref* represents the difference between the measured peak position and the reference (1 bar) peak position, at the reference *T* of 25 °C.

Inclusion *P’s* for quartz inclusions at room *T* were determined using the *P-*sensitive frequency shift of the ca. 464 cm-1 band according to the following quadratic equation from Ashley et al., 2016, based on the experimental data of Schmidt and Ziemann (2000):

*P* (bar) = (*a* (Δ*ν464*)2*P,Tref*) + (*b* (Δ*ν464*)*P,Tref*)

where a = 4.204 ± 0.81 and b = 1094.5 ± 12 . The parameter (Δ*ν464*)*P,Tref* represents the difference between the measured peak position and the reference (1 bar) peak position, at the reference *T* of 25 °C.

*Pressure correction for quartz inclusions, based on heating experiments*

Prior studies have shown that the quartz-in-garnet thermobarometer may require a correction to account for an apparent (but non-physical) variation in the calculated formation pressure (*P*form) depending on the *T* at which the Raman spectrum was measured (Ashley et al., 2016). Because the inclusions measured in this study are only slightly dilated, we conducted a new heating experiment on a quartz inclusion from northern Scotland (sample MT-09-96 of Ashley et al., 2015b) that is under a nearly identical stress state to correct for our estimated entrapment *P*’s. A single garnet crystal was doubly-polished to ~100-200 μm to ensure no stress relaxation occurs for the analyzed inclusion (see discussion above). Unpolarized Raman spectra of quartz were obtained on a JY Horiba LabRAM HR800 Raman microprobe at Virginia Tech, equipped with a calibrated Linkam THMSG600 heating stage. For instrument set-up and analytical approach, see Ashley et al. (2016). The sample was heated in 50 °C increments to 600 °C; however, the glass window for the heating cell cracked between 400 and 450 °C, with the crack aligned directly over the inclusion. All data collected at T > 400 °C (and during subsequent cooling) is not reliable due to the significant scatter resulting from the laser passing through the cracked window. *P*incl was calculated at each heating step following the approach of Ashley et al. (2016), with the respective entrapment *P* calculated at each step.

At room *T*, the quartz inclusion from sample MT-09-96 has a Δν464 of -0.99 cm-1 relative to a Herkimer quartz standard, which corresponds to a *P*incl of -108 MPa. *P*incl was calculated at each heating step following the approach of Ashley et al. (2016), with the respective entrapment *P* calculated at each step (assuming entrapment *T* of 700 °C, based on estimates by Ashley et al., 2015b; Table A3). We generated a 2nd-order polynomial regression for this entrapment data and used it to correct projected isomekes for the slightly dilated quartz inclusions measured in this study (Table A3; Fig. A1).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| TABLE A4.HEATING EXPERIMENT FOR SAMPLE MT-09-96 TO ALLOW FOR PRESSURE CORRECTION OF THE QUARTZ-IN-GARNET BAROMETER WITH SLIGHTLY DILATED QUARTZ INCLUSIONS. | | | | |
| **Heating T** | **Δν464** | **Pincl,measured** | **Pincl,theory** | **Pform** |
| **(°C)** | **(cm-1)** | **(MPa)** | **(MPa)** | **(MPa)** |
| 27.7 | -0.99 | -108 | -108 | 784 |
| 28.3 | -0.97 | -106 | -107 | 786 |
| 50 | -1.07 | -117 | -95 | 762 |
| 100 | -0.75 | -92 | -69 | 771 |
| 150 | -0.62 | -68 | -41 | 756 |
| 200 | -0.45 | -50 | -10 | 743 |
| 250 | -0.19 | -20 | 23 | 739 |
| 300 | -0.07 | -8 | 59 | 713 |
| 350 | 0.12 | 13 | 98 | 691 |
| 400 | 0.46 | 50 | 143 | 679 |
| *Note: Entrapment pressures are calculated assuming a pure almandine host. Theoretical inclusion pressures are calculated assuming entrapment conditions of 700 °C and 784 MPa. 2nd-order polynomial resulting for formation P at different heating temperatures is: Pform (MPa) = -0.00038(18)·T2 + -0.116(75)·T + 783(6) (R2 = 0.9688), where T is in °C.* | | | | |

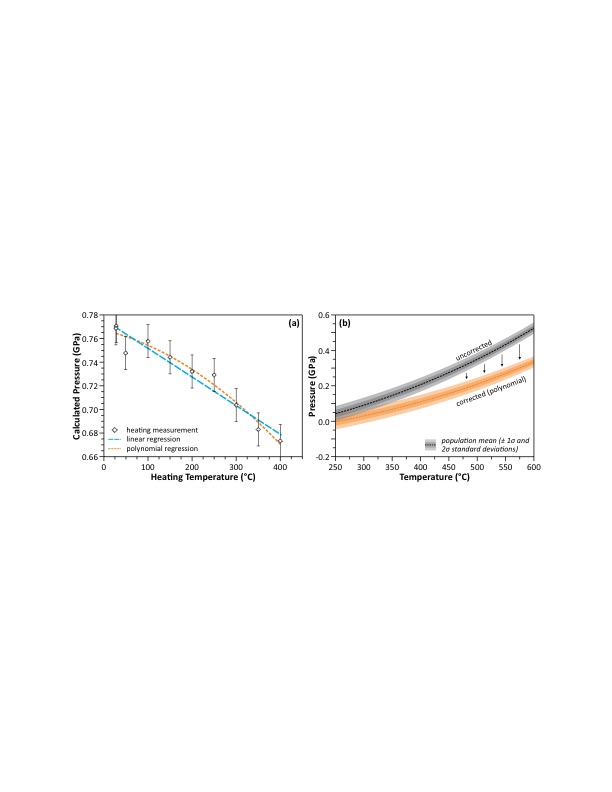


Figure A1: a)Result of the stepwise heating experiment on a pressurized quartz inclusion in garnet, indicating an apparent (non-physical) decrease in the calculated trapping *P* with increasing *T* of the Raman analysis. b) Adjustment of the calculated locus of *P-T* conditions of quartz inclusion trapping consistent with the measured *P*inc, in light of the polynomial regression of the data shown in panel A.

*Estimation of calcium chloride concentration in liquid-rich fluid inclusions*

Regarding the high-density inclusions, results from both Casting Copper and Douglas Hill, and from both garnet- and epidote-hosted inclusions, indicate ice-melting *T*’s (*T*m,ice) of -24.2 to -30.5 °C (Table 4). This range of *T*m,ice is lower than the eutectic *T* of the system H2O-NaCl (-21.2 °C), indicating that the fluid is highly saline and enriched in divalent cation chlorides in addition to NaCl (Steele-MacInnis et al., 2016). Further evidence of enrichment in divalent cations in these inclusions is provided by a few measurements of the approximate first melting (eutectic) *T*, which appear to be always lower than -50 °C (Table 4), indicating that these fluids are likely enriched particularly in CaCl2 (H2O-NaCl-CaCl2 eutectic *T* = -52 °C; Steele-MacInnis et al., 2011), in addition to NaCl. The model of Steele-MacInnis et al. (2011) was used to determine the compositions based on phase equilibria of the system H2O-NaCl-CaCl2. Total salinities for these fluid inclusions ranged from 24.4 to 26.4 wt. % NaCl equivalent. Because the measured *T*m,ice is less than the H2O-NaCl eutectic *T*, this measurement also constrains the minimum concentration of CaCl2 (Fig. A2). Unfortunately, hydrohalite melting could not be unequivocally observed or recorded in these inclusions, and therefore Table 4 reports the permissible range of CaCl2 concentrations based on *T*m,ice. Salinities ranged from 1.3 to 15.9 wt. % NaCl and 8.5 to 23.8 wt. % CaCl2 (Table 4; Fig. A2), confirming that these high-density inclusions are highly enriched in divalent cations, particularly CaCl2.



Figure A2. Ternary diagram illustrating potential compositional ranges of salinities, based on *T*m of iceand *T*m of hydrohalite. Realistic salinities can lie anywhere along each tie line connecting the end-member compositions represented by the red dots. The shaded blue region shows the full range of possible salinities exhibited in these samples. Fields and boundaries are labeled with the phases that are present within and along them.

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