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Accurate and precise quantification of major and trace element compositions of calcic-sodic fluid inclusions by combined microthermometry and LA-ICPMS analysis

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Abstract

Determination of absolute trace-element concentrations in fluid inclusions using laser-ablation (LA) ICPMS requires an internal standard, i.e., the concentration of one element must be independently known from independent observation. Microthermometric determination of the last melting temperature of ice, hydrohalite or halite is routinely used to calculate apparent salinities in wt% NaCl equivalent, using phase relations in the binary H₂O-NaCl system to estimate Na concentration. Calculating the concentrations of all other elements requires an empirical correction, if additional salt concentrations are of similar magnitude as that of NaCl. If CaCl₂ is the main additional salt component, as in many low-temperature basin and basement brines, absolute Na concentrations (wt% NaCl abs.) can be obtained by observing two melting temperatures (hydrohalite and either ice or halite), uniquely defining the major element composition of the fluid in the ternary model system H₂O – NaCl – CaCl₂ and allowing Na to be used as internal standard for quantifying all minor and trace elements. Test results for a range of compositions show that calcium concentration can be determined more precisely by microthermometry than by LA-ICPMS analysis, but that both methods agree within error. The combined approach of microthermometry and LA-ICPMS analysis described here permits reliable quantification of major (Ca, Na) as well as trace element concentrations in sodic-calcic brine inclusions, even in Ca-rich host minerals such as fluorite or Ca-bearing carbonates.

Keywords: *fluid inclusions; microthermometry; laser ablation ICPMS; calcic brines; quantification, IOCG, internal standard, NaCl equiv., NaCl abs.*

1. Introduction

Low-temperature hydrothermal brines commonly contain CaCl₂ and NaCl as dominant salt components, such that fluid inclusions (FI) are approximately described by the ternary H₂O-NaCl-CaCl₂ system (Fritz and Frape, 1982; McKibben et al., 1988). Such calcic-sodic brines occur as fluid inclusions in various mineral deposits such as Mississippi valley-type lead-zinc deposits (Richardson and Pinckney, 1984; Haynes and Kesler, 1987; Shelton et al., 1992; Stoffell et al., 2008), unconformity-related uranium deposits (Wilde et al., 1989; Derome et al., 2005; Shepherd et al., 2005) and in iron-oxide Cu-Au (IOCG)-type deposits (Xu, 2000; Mark et al., 2005; Davidson et al., 2007; Baker et al., 2008; Bertelli and Baker, 2010) including giant Olympic Dam

in South Australia (Oreskes and Einaudi, 1992). In addition, fluids in various other geologic settings are commonly calcic-sodic, for example sedimentary-basinal brines (Zwart and Touret, 1994; Lowenstein et al., 2003; Schmidt Mumm and Wolfgramm, 2004; Mercadier et al., 2010), groundwater in cratonic basement rocks (Bottomley et al., 1999), sub-seafloor hydrothermal fluids (Vanko et al., 1992), fluids in mafic pegmatoids cutting layered mafic intrusions (Schiffries, 1990), late brines trapped in Archean gold veins (Robert and Kelly, 1987), low temperature hydrothermal Au, Pt, Pd $\pm$ U mineralization (Mernagh et al., 1994) and porphyry copper deposits (Dilles and Einaudi, 1992; Klemm et al. 2007).

The first-melting temperature (i.e., the eutectic temperature) observed during microthermometry gives an indication of the appropriate fluid system to interpret the composition of natural fluids within fluid inclusions. Vapour-saturated CaCl_2 -NaCl-bearing inclusions show distinctive freezing and heating behaviour during low-temperature microthermometry. After undercooling below -80°C , the liquid changes instantaneously to a brown-orange mosaic of unidentifiable micro-crystals. Slow heating results in crystal coarsening until first melting can be observed close to the ternary eutectic temperature at -52°C (Yanatieva, 1946). Owing to the difficulty of observing the precise first-melting temperature in fluid inclusions, NaCl- CaCl_2 -bearing fluids can be inferred if first melting occurs somewhere between -54°C and -47°C (Zwart and Touret, 1994). The melting temperatures of the last *and* the next-to-last solid phases determine the bulk composition of the fluid (Haynes, 1985; Heinrich et al., 1989; Schiffries, 1990; Vanko et al., 1992; Steele-MacInnis et al., 2011). Complete descriptions of possible melting paths in the H_2O -NaCl- CaCl_2 system are described elsewhere, including possible difficulties arising from metastability (Schiffries, 1990; Steele-MacInnis et al., 2011). Estimates of bulk fluid composition can be obtained using non-destructive methods like graphically displayed phase equilibrium data obtained from microthermometry (Robert and Kelly, 1987; Vanko et al., 1988; Vanko et al., 1992), or semi-quantitative Raman spectroscopy (Mernagh and Wilde, 1989; Derome et al., 2003; Guillaume et al., 2003).

An overview of thermodynamic and numerical models to estimate compositions in the H_2O -NaCl- CaCl_2 fluid system is given by Steele-MacInnis et al. (2011) and references therein. LA-ICPMS is a powerful technique for fast and accurate microanalysis of major and trace-element ratios in individual fluid inclusions, but absolute quantification of concentrations requires an internal standard, i.e., one element with known concentration obtained from an independent measurement or estimation (Günther et al., 1998; Heinrich et al., 2003). The most commonly used internal standard in fluid-inclusion LA-ICPMS analysis is sodium, usually obtained by prior microthermometry. To measure sodium concentration, melting temperatures of ice, hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) and/or halite are used to compute apparent salinities of FI, using the known phase equilibria of the binary H_2O -NaCl system (Bodnar and Vityk, 1994). For more complex fluids containing salts other than NaCl, an empirical salt correction (Heinrich et al., 1992, 2003) is used to account for additional salts detected by LA-ICPMS, but the accuracy of this correction cannot be tested for each case.

A mathematical description of phase relations in the H_2O -NaCl- CaCl_2 fluid system has recently been presented by Steele-MacInnis et al. (2011). We have implemented these equations into the SILLS software for LA-ICPMS signal reduction (Guillong et al., 2008), providing the basis to accurately determine trace element concentrations in FI using wt% NaCl abs. as a precise internal standard. This paper describes the procedure to obtain wt% NaCl abs. in Ca-Na-bearing brines and tests the improved accuracy of trace element concentrations determined by LA-ICPMS.

2. Analytical setup and sample description

We performed careful petrography to select assemblages of multiple coeval Ca-Na bearing fluid inclusions (FIA = group of fluid inclusions with consistent phase proportions entrapped at the same time, e.g., along a single fracture plane or growth zone; Goldstein and

Reynolds, 1994). Samples originate from the Prominent Hill (PH) iron-oxide Cu-Au (IOCG) deposit in South Australia and from the low-grade metamorphic base-metal district of Mt. Isa (MTI) in northern Queensland. The fluid inclusions were hosted in quartz or fluorite. Inclusion petrography and microthermometry were conducted using an Olympus BX60 transmitted light microscope and a Linkham heating-freezing stage. The LA-ICPMS setup described in Günther et al. (1998) and Heinrich et al. (2003) was used to determine trace element ratios, parameters are shown in Table 1.

Table 1. Instrumental parameters of the LA-ICPMS and microthermometry systems used in this study.

LA-ICPMS System	
Laser type	ArF excimer laser (193nm) (Coherent, Germany) with homogenized beam path
Laser energy for mineral ablation	>30J/cm ²
Laser pulse frequency	10Hz
Ablation diameter	variable from 5 to 100µm by adjusting a variable aperture
ICPMS system	Elan 6100 DRC ICP quadrupole mass Spectrometer from Perkin Elmer
Carrier gas	He, 1.1 l/min
Auxiliary gas	H ₂ 5ml/min
Dwell time	10ms except for Ca:20ms
External std	NIST610
Microthermometry System	
Heating-freezing stage	Linkham THMSG 600 heating - freezing stage
controlling units	Linkham LNP and CI 94
Optical microscope	Nikon Eclipse E600 Pol
Objective	50x
Calibration standard	Syn FliC® fluid inclusion H ₂ O (0° and 374.1°C), H ₂ O-CO ₂ (-56.6°C)

Five different fluid inclusion types were classified according to phase proportions, number and appearance of daughter crystals, inclusion shape and type of host mineral. All five inclusion types described below contain liquid and vapour at room temperature, although they have distinctly variable volume proportions of vapour, and some also consistently contain halite or other small solid phases. In the terminology used here, fluid inclusion types are abbreviated by their room-temperature phases, with capital letters standing for liquid (L), vapour (V_x, the subscript x indicates the volume % of vapour), halite (H) or other solid phase(s) (S). Four of the five inclusion types are found at Prominent Hill. These include types LV₅, LV₁₀S and LV₂₀S, which were fluorite-hosted FI in calcite-fluorite-barite±chalcopyrite veins. These FIA occasionally occurred as pseudo-secondary trails (LV₁₀S), but were mostly secondary trails and clusters. LV₁₀S and LV₂₀S were equant and angular in shape and had diameters between 6 and 30 µm. LV₅ had irregular shape and variable sizes between 8 and 100 µm. Type LV₅HS assemblages were from quartz in siderite-quartz-chalcopyrite veins, occurring as primary and pseudo-secondary FIA, with consistent sub-rounded shapes and diameters between 5 to 25 µm. A LV₁₀ inclusion assemblage originated from a large locally vuggy late-metamorphic quartz vein associated with regional alteration of metabasalts in the Mt. Isa district (Heinrich et al., 1995). Inclusions have irregular shapes, were likely pseudo-secondary and between 5 and 45 µm in diameter. Using the approach detailed in Steele-MacInnis et al (2011), CaCl₂ and NaCl concentrations were calculated from 45 inclusions in 10 individual FIA, based on melting temperatures of solid phases measured by microthermometry.

Element concentration ratios of K, Mn, Fe, Cs, Pb and Ca with respect to Na were analysed in 45 individual inclusions using LA-ICPMS. The SILLIS software package from the

University of Leeds and ETH Zürich was used for data reduction (Allan et al., 2005, Guillong et al., 2008), including element spike elimination and time integration of background-subtracted, host-corrected FI signals. Each ablation was monitored continually using a transmitted light microscope and as real-time signal from the mass spectrometer, to determine the part of the signal representing the ablated inclusion, such that the fluid inclusion signal could be isolated for integration. Transient LA-ICPMS signals were inspected for each element and considered significant if integrated intensity was above the limit of detection (LOD) of $3\sigma_{\text{background}}$ (Longerich et al. 1996) and showed an identifiable peak in the data acquisition window.

3. Analytical procedure and results

3.1 Low temperature microthermometry

The melting sequence (Fig. 1) and temperatures of ice, hydrohalite and halite hosted in selected FIA in quartz and fluorite from Prominent Hill and quartz from Mt. Isa indicated Ca^{2+} and Na^+ as major cations. This was confirmed by the LA-ICPMS data, showing that additional cations (e.g. K, Fe, etc.) were usually less than one fifth of the Na concentration. Thus, we interpreted the measured melting temperatures using the phase equilibria for $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ assuming that effects of those minor cations on the microthermometric measurements are small. With careful cyclic heating and cooling (Haynes, 1985), individual last melting temperatures of ice, hydrohalite and halite could each be measured reliably, within a typical reproducibility of $\pm 0.2^\circ\text{C}$ or better. Salinities in the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system were calculated from combinations of the temperatures of either final melting of ice and hydrohalite, or melting of ice and final dissolution of halite. These measured values were then used as input parameters in a Microsoft® Excel-based calculation sheet, based on the empirical model of Steele-MacInnis et al. (2011). The model uses a set of equations describing the liquidus surface and cotectic melting curves in parts of the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ phase diagram. Depending on the observed melting phases and their final melting temperature during microthermometry the model uses two phase melting temperatures as input parameters and yields estimates of total salinity as well as independent CaCl_2 and NaCl concentrations within each individual inclusion.

Low-temperature microthermometry of vapour-saturated CaCl_2 -NaCl-bearing FI showed a distinctive freezing and heating behaviour (Fig. 1a-e). Upon freezing, the liquid changed instantaneously into an orange-brown microgranular mass (Fig. 1c). Heating resulted in coarsening of still unidentifiable crystals (Fig. 1d). A clearly visible liquid phase was usually observed by heating up to -48°C . With further melting, ice crystals became transparent with a clear relief against their host and were therefore easy to recognise (Fig. 1e). Hydrohalite appeared as a greenish and birefringent solid (Fig. 1e). During heating, FI may have either ice, hydrohalite or halite as the last melting (liquidus) phase (Fig. 2a-c). Observed melting paths are described below, where T_{m1} and T_{m2} denote the temperature of the second-to-last and last solid phases to melt, respectively. Whether the second-to-last or last phase to melt is ice, hydrohalite or halite depends on the bulk composition of the fluid. The combination of T_{m1} and T_{m2} can be used to uniquely determine the bulk fluid composition in the $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system (Fig. 2). In all the FI studied here, the first solid to melt at the ternary eutectic was likely antarcticite (Fig. 2a). Further heating lead to melting of ice and hydrohalite along the ice-hydrohalite cotectic curve.

Figure 1. Typical freezing and melting behavior of Ca-Na-dominated fluids (cf. Zwart and Touret, 1994). **A:** Fluid inclusion assemblage at 25°C; **B:** single inclusion at 20°C; **C:** -100°C, distinct freezing behavior showing brown- orange tint; **D:** -44°C, crystal grain coarsening of ice and hydrohalite after passing the eutectic temperature at -52°C; **E:** cotectic melting of ice and hydrohalite single crystals at -29°C.

Figure 2. Observed melting paths in the ternary diagram H₂O-NaCl-CaCl₂ (modified after Steele-MacInnis et al., 2011) for three bulk compositions represented in the test assemblages. See text for discussion.

Inclusions with bulk composition in the field of the ice liquidus displayed complete cotectic melting of hydrohalite (Fig. 2a, T_{m1}). As temperature was increased above T_{m1} , the liquid composition evolved toward the H_2O apex until all ice was molten, defining the bulk fluid composition in the ternary system (Fig. 2a, T_{m2}). Inclusions of this type required particularly careful measurement because they contained only a small amount of hydrohalite when frozen, such that there was little hydrohalite to melt along the cotectic line. Frozen inclusions of this type were heated until only one small ice crystal remained. By re-cooling down from this temperature, this small “seed” crystal could be grown into a large single crystal of ice. At $-100\text{ }^{\circ}\text{C}$, the inclusions were completely frozen again showing one large ice crystal filling a large proportion of the inclusion volume. Slow heating toward the eutectic (at a maximum heating rate of $\leq 5\text{ }^{\circ}\text{C}/\text{min}$) prevented formation of the mosaic texture, which limits the visibility of phase transitions. After increasing temperature above the eutectic, heating at a rate of $\leq 0.5\text{ }^{\circ}\text{C}/\text{min}$ usually led to formation of visible hydrohalite crystals, which gradually merged to measurable crystal sizes. Alternatively, careful heating and cooling around the eutectic led to coalescence of small hydrohalite crystals. In both cases, the final melting temperature of the hydrohalite crystal could then be measured.

For inclusions with bulk compositions in the liquidus field of hydrohalite (Fig. 2b), ice melted before hydrohalite on the cotectic, and therefore T_{m1} represented the melting temperature of ice. Leaving the cotectic line upon further heating, the liquid composition in the inclusion evolved directly towards the composition of hydrohalite until all remaining hydrohalite finally melted (Fig. 2b, T_{m2}). When ice was consumed before hydrohalite, the subsequent melting of hydrohalite crystals could usually be observed relatively easily. Otherwise, slow heating rates of ≤ 1 to $2\text{ }^{\circ}\text{C}/\text{min}$ were used to allow the small remaining hydrohalite crystals to merge. Sometimes accretion of hydrohalite crystals was slow or the final hydrohalite melting temperature occurred close to the ice melting temperature. Both of these phenomena made observation of hydrohalite melting difficult. In those cases, holding the temperature constant just above T_{m1} for a few minutes led to coalescence of the remaining hydrohalite crystals. Hydrohalite melting could then be observed accurately. In practice, hydrohalite can sometimes disappear above the 0.1°C peritectic of $\text{NaCl-H}_2\text{O}$, indicating metastable melting behaviour (Zwart and Touret, 1994; Steele-MacInnis et al., 2011). FI showing such metastable melting were not included in this study.

Inclusions with bulk compositions in the halite liquidus field (Fig. 2c) showed a somewhat different evolution. After leaving the eutectic with complete consumption of antarcticite, ice was the next phase to disappear along the ice-hydrohalite cotectic line (Fig. 2c, T_{m1}). Again the composition evolved straight toward the hydrohalite composition, but in this case intersected the hydrohalite-halite peritectic phase boundary. Hydrohalite was converted into halite during heating while releasing chemically bonded water (Fig. 2c, T_a). With further heating, the liquid composition evolved directly towards halite until the last halite crystal dissolved completely during heating runs (Fig. 2c, T_{m2}). Melting of hydrohalite was sometimes sluggish or delayed due to metastability. Thus, for FI in the halite liquidus field, next-to-last melting (namely hydrohalite melting or peritectic phase-conversion temperatures) was not used for salinity determination. Instead, combinations of the final ice melting with the corresponding final halite dissolution temperature were used to determine fluid bulk composition. This is shown graphically in Figure 2c.

Fluid inclusions used in this study include only those in which at least one phase was clearly identified and its melting temperature was precisely measured by microthermometry. However, it was not always possible to observe *both* ice melting *and* its corresponding hydrohalite/halite melting in every individual inclusion within an FIA. For inclusions for which one or the other melting temperature could not be observed, the average melting temperature from successful measurements within the same FIA were used to replace the missing melting temperature. This approach is based on the principle that fluid inclusions within a homogeneously trapped fluid inclusion assemblage should have the same composition and the

same microthermometric behaviour, provided that they were trapped as a single homogeneous phase and were not modified by post-entrapment processes. Applying this procedure to our dataset is justified because the FIA have consistent phase ratios *and* the microthermometric measurements within each FIA were generally very consistent (mostly within less than ± 1 °C; in two cases up to ± 3 °C, and only in one case up to ± 6 °C for ice and hydrohalite; up to ± 9 °C for halite; Table 2). Using this procedure, the composition of each FI was computed individually, allowing an estimate of overall analytical uncertainty for each fluid sample represented by an inclusion assemblage.

Table 2. Microthermometric data and CaCl₂-NaCl salinity from selected fluid inclusions from Prominent Hill (PH-sample no. 15.2, 82 and 98.2) and Mount Isa (MTI sample-no. 73529 in used in Heinrich et al., 1995). Salinity calculated based on combined final ice and hydrohalite melting or ice melting and final halite dissolution temperatures using the model of Steele-MacInnis et al. (2011). Data exclude measurements of metastable hydrohalite melting. The number in the parentheses is the number of measured inclusions for the average.

Sample	FIA / #	µm	first melt -52 to -	Tm(ice)	Tm(HH)	Tm(H)	wt%	wt%	wt%	wt%	wt%	Ca/(Ca+N)
PH98.2_ LV10S	FIA			-26.4 ± 1.7	-5.7 ± 0.6 (7)							
	2	22	x	-25.9	-6.6		15.3	11.6	16.7	6.0	4.2	0.41
	4	18	x	-26.0	-5.4		15.2	11.7	16.7	6.0	4.2	0.41
	7	14	x	-26.0	-6.3		15.2	11.7	16.7	6.0	4.2	0.41
	12	12	x	-26.4 ^a	-5.8		14.6	12.4	16.8	5.7	4.5	0.44
PH98.2_ LV5_1	FIA			-6.4 ± 0.8 (4)	-24.0 ± 0.1							
	1	24	x	-6.0	-23.9		6.4	3.1	5.9	2.5	1.1	0.31
	2	100	x	-6.5	-24.0		6.8	3.4	6.3	2.7	1.2	0.31
PH98.2_ LV5_3	FIA			-6.1 ± 0.8 (6)	-25.0 ± 0.0							
	2	80	x	-5.6	-25.0 ^a		5.3	3.8	5.6	2.1	1.4	0.40
	5	80	x	-6.1 ^a	-25.0		5.6	4.1	6.0	2.2	1.5	0.40
PH82_ LV20S_1	FIA			-30.6 ± 1.2	-17.4 ± 5.4							
	1	28	x	-29.3	-22.0		9.4	17.2	16.7	3.7	6.2	0.63
	3	28	x	-31.5	-17.4 ^a		8.2	19.4	17.4	3.2	7.0	0.68
	5	34	x	-28.5	-25.6		9.7	16.3	16.3	3.8	5.9	0.61
	15	19	x	-30.0	-17.4 ^a		9.4	17.8	17.0	3.7	6.4	0.64
	17	14	x	-30.9	-17.4 ^a		8.6	18.8	17.2	3.4	6.8	0.67
PH15.2_ LV5HS_1	FIA			-27.4 ± 0.6	16.1 ± 2.9 (3)	258.7 ± 8.6						
	1	20	x	-27.5	16.3	267.5	27.8	9.9	23.2	11.0	3.6	0.25
	2	13	x	-27.7	18.8	258.7 ^a	26.9	10.3	22.9	10.6	3.7	0.26
	3	12	x	-27.4 ^a		254.2	26.6	10.2	22.6	10.5	3.7	0.26
	4	24	x	-27.4		258.7 ^a	27.0	10.0	22.8	10.6	3.6	0.25
	5	8	x	-27.4 ^a		263.2	27.5	9.9	23.0	10.8	3.6	0.25
	6	20	x	-26.4	13.1	246.0	26.5	9.3	22.0	10.4	3.4	0.24
PH15.2_ LV5HS_2	FIA			-27.4 ± 0.0	14.7 ± 0.3 (2)	260.6 ± 4.6						
	2	22	x	-27.4 ^a	14.5	268.2	28.0	9.8	23.2	11.0	3.5	0.24
	3	20	x	-27.4		254.1	26.6	10.2	22.6	10.5	3.7	0.26
	6	12	x	-27.4		260.6 ^a	27.2	10.0	22.9	10.7	3.6	0.25
	8	10	x	-27.4 ^a		259.4	27.1	10.0	22.8	10.7	3.6	0.25
	9	11	x	-27.4 ^a		261.2	27.3	10.0	22.9	10.7	3.6	0.25
	10	10	x	-27.4 ^a		261.9	27.3	10.0	23.0	10.8	3.6	0.25
	11	8	x	-27.4 ^a		258.6	27.0	10.1	22.8	10.6	3.6	0.25
PH15.2_ LV5HS_4	FIA			-32.2 ± 1.9		267.1 ± 4.6						
	1	22	x	-34.4		267.1 ^a	25.6	14.3	24.7	10.1	5.2	0.34
	2	14	x	-31.1		263.7	26.0	12.7	23.9	10.2	4.6	0.31
	3	12	x	-31.1		272.4	26.9	12.4	24.3	10.6	4.5	0.30
	5	10	x	-32.2 ^a		265.3	25.9	13.3	24.2	10.2	4.8	0.32
MTI_ LV10_2	FIA			-23.6 ± 1.0	-11.0 ± 1.2							
	1	44	x	-23.2	-9.2		20.1	5.8	15.9	7.9	2.1	0.21
	3	24	x	-23.2	-11.1		19.8	5.8	15.8	7.8	2.1	0.21
	8	12	x	-23.3	-11.9		19.5	6.1	15.7	7.7	2.2	0.22
	9	10	x	-23.6	-11.0 ^a		19.0	6.8	15.9	7.5	2.5	0.25
MTI_ LV10_4	FIA			-23.0 ± 0.4	-23.2 ± 0.2							
	1	35	x	-23.1	-23.2		17.9	6.1	14.7	7.0	2.2	0.24
	3	30	x	-23.2	-22.7		18.0	6.1	14.8	7.1	2.2	0.24
	4	27	x	-23.4	-23.4		17.5	6.6	14.8	6.9	2.4	0.26
	5	12	x	-22.4	-23.2		17.5	6.0	14.5	6.9	2.2	0.24
	6	7	x	-22.4	-23.2		17.5	6.0	14.5	6.9	2.2	0.24
	7	10	x	-23.1	-23.2		17.9	6.1	14.7	7.0	2.2	0.24

Table 2. (continued)

Sample	FIA / #	μm	first melt -52 to -	Tm(ice)	Tm(HH)	Tm(H)	wt%	wt%	wt%	wt%	wt%	Ca/(Ca+N)
MTI_	FIA			-23.5 ± 0.3	-12.4 ± 0.2							
LV10_6	2	22	x	-24.1	-12.3		17.8	8.1	15.9	7.0	2.9	0.29
	4	18	x	-23.5	-12.3		19.0	6.6	15.8	7.5	2.4	0.24
	5	26	x	-23.2	-12.5		19.7	5.9	15.7	7.7	2.1	0.22
	6	20	x	-23.4	-12.3		19.2	6.4	15.7	7.6	2.3	0.23
	9	12	x	-23.4	-12.4 ^a		19.2	6.4	15.7	7.6	2.3	0.23

^a FI showed either metastable melting of one phase, or final melting was not observed. In both cases the FIA average temperature of the respective phase was used to calculate the individual FI salinity.

3.2 Composition in the H₂O-NaCl-CaCl₂ ternary system

Results were calculated in terms of weight concentrations of NaCl, CaCl₂, total salinity (chloride equivalent, S_{cr}), absolute Na⁺ and Ca²⁺ concentrations and Ca/(Na+Ca) proportions (Table 2). Calculated salinities exclude any data obtained from metastable melting behaviour. In general, fluid inclusions used in this study showed a range of assemblage-averaged Ca/(Ca+Na) from 0.22 ± 0.02 to 0.63 ± 0.03 (Table 2, Fig. 3).

Figure 3. Ternary diagram showing H₂O-NaCl-CaCl₂ fluid composition of selected fluid inclusion from Prominent Hill and Mount Isa based on microthermometry. Open symbols indicate FI within an assemblage where microthermometry measurements required the use of an average value for the final melting temperature of one of the phases, based on other inclusions in the same assemblage (either ice, hydrohalite or halite).

3.3 Major and trace element composition determined by LA-ICPMS

Combined results from microthermometry and LA-ICPMS analysis are reported in Table 3 and in Figure 4, showing individual FI compositions, including LOD for elements determined by LA-ICPMS. LA-ICPMS data showing element concentrations below the LOD were marked as “< LOD”. The inclusions are sorted by decreasing sodium content within each FIA. In general, all inclusion types contained major amounts of Na and Ca and lesser amounts of K and Fe, Mn, Pb and Cs. LA-ICPMS data thus confirm the assumption that Na and Ca are the dominant cations. Only the K concentrations in a few individual FI within some FIA approach the measured Ca contents (e.g. PH15.2_LV5H_2 inclusion 1 and 2, MTI_LV10_2 inclusion 3 and MTI_LV10_4 inclusion 6) (Table 2) but this is at least partly explained by the large scatter in the Ca and K peak intensities. Owing to lack of experimental data, no attempt was made to correct for the influence of minor salts on phase relations in the ternary H₂O-NaCl-CaCl₂ fluid system.

Table 3. Fluid inclusion major and trace element composition determined with LA-ICPMS and microthermometry for selected assemblages from Prominent Hill (PH-sample no 15.2, 82 and 98.2) and Mount Isa (MTI sample-no. 73529 in used in Heinrich et al., 1995). Abbreviations: n.i. = not included due to insufficient signal detection (SILLS quantification resulting in concentration above the 3 σ value but without a visible peak justifying the element quantification); MT = results from microthermometry; LA = results from laser ablation ICPMS; LOD = limit of detection]

FIA- Sample	FI	μm	Value (ppm)		Ca (MT)	Ca (LA)	Mn	Fe	Cs	Pb	LOD (ppm)						
			Na	K							Na	K	Ca	Mn	Fe	Cs	Pb
PH98.2_ LV10S	2	22	60100	2700	41800	n.i.	n.i.	2340	3.0	39	19	225	15400	14	213	0.2	1.1
	4	18	60100	<409	42300	n.i.	181	<380	7.6	n.i.	26	409	27000	24	380	0.3	2.2
	7	14	59300	<9110	42400	<580000	n.i.	<7600	<11	<53	118	9110	580000	512	7600	11	53
	12	12	57500	4130	44900	n.i.	<11	<167	2.2	n.i.	3.0	183	12000	11	167	0.3	1.1
PH98.2_ LV5_1	1	24	25200	<459	11200	<32500	<26	<393	n.i.	<2.4	9.9	460	32500	26	393	0.3	2.4
	2	100	26400	<118	12300	n.i.	<6.7	<101	0.7	1.2	2.3	119	8170	6.7	101	0.1	0.6
PH98.2_ LV5_3	2	80	20800	196	13900	n.i.	<9.3	n.i.	n.i.	n.i.	3.6	169	11300	9.3	126	0.3	0.9
	5	80	22300	<428	14800	<96500	<75	1260	10	241	19	1430	96500	75	1214	2.1	6.7
PH82_ LV20S_12	1	28	37100	3800	61900	n.i.	<5.0	1320	5.0	19	6.9	140	8390	5.0	111	0.2	0.4
	3	28	32600	<3280	69900	<195000	<114	11300	12	<8.8	130	3280	195000	114	2570	2.3	8.8
	5	34	38600	4350	58600	n.i.	511	521	7.8	51	9.4	233	13900	8.1	183	0.2	0.7
	15	19	37100	<3300	64300	<194000	752	11200	<2.5	103	20	3300	194000	114	2630	2.5	10
	17	14	34100	n.i.	67800	<216000	507	12200	3.0	52	22	3690	216000	128	2930	2.7	11
PH15.2_ LV5HS_1	1	20	109800	19600	35700	<15300	1110	17600	117	1500	3.9	233	15300	22	254	0.4	1.7
	2	13	105300	11800	37300	n.i.	884	12700	51	1500	4.9	524	34400	49	578	0.7	2.9
	3	12	104600	21800	36700	<61800	925	17700	92	2030	8.1	935	61800	88	1040	1.4	4.5
	4	24	106100	15000	36300	33600	417	4540	79	1430	1.2	82	5420	7.7	91	0.1	0.5
	5	8	108300	11100	35800	n.i.	785	19600	61	1680	14	1090	73900	48	905	1.1	4.9
	6	20	104600	17800	33600	23272	n.i.	n.i.	100	1290	0.4	35	2320	3.4	37	0.1	0.2
PH15.2_ LV5HS_2	2	22	109800	32400	35300	27100	849	6160	193	861	1.7	204	13300	19	221	0.3	1.5
	3	20	104600	26700	36700	n.i.	572	2795	149	2120	4.8	345	22600	32	351	0.6	3.1
	6	12	106800	14800	36100	n.i.	932	14200	91	1820	5.8	623	40900	58	704	1.0	4.3
	8	10	106800	43800	36200	n.i.	2530	67500	65	1370	16	668	45700	29	632	0.6	3.9
	9	11	107600	12400	36000	n.i.	775	16800	83	1300	19	1640	112000	71	1470	2.0	8.0
	10	10	107600	21400	36000	n.i.	899	19700	77	1250	61	2090	142000	91	1790	2.4	14
	11	8	106100	12200	36300	<82700	127	3160	44	779	26	1220	82700	53	1040	1.4	7.4
PH15.2_ LV5HS_4	1	22	100900	17300	51700	28200	660	9980	93	1385	13	286	19500	13	258	0.2	2.0
	2	14	102400	20000	46000	<29600	700	10000	90	726	12	434	29600	19	379	0.6	2.2
	3	12	106100	20100	44800	<38400	970	16200	98	1610	14	564	38400	24	491	0.7	2.7
	5	10	101600	17100	48100	<395000	775	<5190	137	2370	59	5800	395000	240	5390	2.1	27
MTI_ LV10_2	1	44	79000	12000	21000	16000	308	485	162	49	0.8	14	718	5.3	86	0.1	0.4
	3	24	78000	15200	21100	17600	544	1120	192	66	7.0	72	3060	25	371	0.5	1.1
	8	12	76800	11600	22100	13800	259	1350	131	45	7.2	95	4320	35	412	1.0	2.4
	9	10	74700	4400	24700	<10700	<96	<1072	125	24	118	248	10700	96	1070	2.1	6.8

Table 3. (continued)

FIA- Sample	FI	μm	Value (ppm)								LOD (ppm)						
			Na	K	Ca (MT)	Ca (LA)	Mn	Fe	Cs	Pb	Na	K	Ca	Mn	Fe	Cs	Pb
MTI_ LV10_4	1	35	70400	13300	22000	21200	266	384	174	24	3.1	39	1640	14	179	0.3	0.9
	3	30	70900	13000	22000	20900	<147	4080	86	200	40	388	16100	147	1960	3.4	13
	4	27	68800	14300	24000	38400	287	<848	174	53	19	175	7500	63	848	0.9	3.5
	5	12	69000	9600	21600	18600	n.i	<1880	131	16	31	480	20300	177	2500	5.0	12
	6	7	69000	20200	21600	22700	<102	<1379	110	22	21	277	11700	102	1379	2.5	6.4
	7	10	70400	11500	22000	28900	354	4440	141	22	14	193	8270	76	1044	1.9	4.8
MTI_ LV10_6	2	22	70000	10200	29100	50400	<285	<3250	n.i.	<16	57	747	31400	285	3250	9.5	16
	4	18	74900	11600	23900	<20800	228	2530	126	13	37	470	20800	175	1640	4.3	10
	5	26	77300	10000	21200	11400	195	<605	135	<3.3	8.5	110	4970	42	605	1.2	3.3
	6	20	75700	13500	23000	39900	n.i.	<774	n.i.	n.i.	10	153	6480	58	774	2.0	1.6
	9	12	75700	8840	23000	<31900	<278	<3330	37	38	56	732	31900	278	3330	6.4	12

Figure 4. Major and trace element concentrations of FI from Prominent Hill and Mount Isa samples. Dashed lines separate petrographic assemblages. Open symbols of Na, Ca and total salinity S[Cl] indicate microthermometry derived salinities where one average phase melting temperature of the FIA (either ice, hydrohalite or halite) during microthermometry has been used to determine the inclusions salinity. Note the more precise determination of Ca by microthermometry. Other elements (K, Fe Mn, Pb and Cs) were quantified from LA-ICPMS signals in SILLS software using wt% NaCl abs. as internal standard, confirming that these elements are present in lesser concentrations justifying use of the ternary model system for internal standardisation. Horizontal stripes mark limits of detection for each element in the LA-ICPMS analysis

The greatest source of potential error in this procedure lies in any misinterpretation of the phase types (confusion of ice and

hydrohalite) during microthermometry. This would lead to dramatically incorrect salinities and element concentrations determined by LA-ICPMS, as illustrated by the following examples. If during microthermometry in FIA PH98.2_LV₁₀S (Table 2 and 4) the final melting temperature were erroneously assigned to ice melting instead of assigning it correctly to hydrohalite melting, the calculated salinity in NaCl eq. (Bodnar and Vityk, 1994) of would be underestimated by ~40% and therefore lead to significantly lower element concentrations determined by LA-ICPMS (Table 4). In contrast, observing only final ice melting in FIA PH98.2_LV₅_1, the corresponding NaCl eq. would be more than 40% higher than NaCl abs. (Table 4) resulting in overestimation of trace elements during LA-ICPMS analysis. Lesser but still systematic errors result from measuring halite dissolution without observation of hydrohalite melting, e.g. in FIA PH15.2_LV₅HS_2, using only NaCl eq. concentration derived from the observed halite dissolution temperature of ~260 °C leads to NaCl eq. of 35% wt, compared to NaCl abs. of ~27% wt. Neglecting the effect of Ca during microthermometry incorrectly increases the concentrations of all trace elements determined by LA-ICPMS by ~30% (Table 4) in this FIA. If in FIA PH15.2_LV₅HS_2 NaCl eq. is used as internal standard in combination with the empirical salt correction (Heinrich et al. 1992, 2003) for K with K/Na > 0.1 and the effect of Ca is neglected because of the difficulties of low count rates and high backgrounds on Ca, the error is overall smaller but elements are still overestimated ~20% compared to NaCl abs. internal standardisation (Table 5). Thus, identification of the applicable fluid system and careful microthermometry of two phase transitions can avoid this systematic error and lead to more reliable element concentrations determined by LA-ICPMS.

Table 4. Examples illustrating differences of calculated internal standards for LA-ICPMS element quantification using salinity data (NaCl abs.) obtained from observation of two phase melting in the H₂O-NaCl-CaCl₂ system and internal standard obtained from misinterpreted microthermometric phase melting temperatures using NaCl- H₂O fluid system (see text for details). The number in the parentheses is the number of measured inclusions for the average.

Sample	FIA /	µm	Tm(ice)	Tm(HH)	Tm(H)	wt% NaCl Steele-MacInnis et al. (2011)	wt% CaCl ₂	wt% NaCl eq. Bodnar + Vityk	Difference of NaCl from NaCl abs. in %
PH98.2_ LV10S	FIA		-26.4 ± 1.7	-5.7 ± 0.7 (6)					
	2	22	-25.9	-6.6		15.3	11.6	10.0	-34.5
	4	18	-26.0	-5.4		15.2	11.7	8.4	-45.0
	7	14	-26.0	-6.3		15.2	11.7	9.6	-36.4
	12	12	-26.4 ^a	-5.8		14.6	12.4	9.0	-38.4
PH98.2_ LV5_1	FIA		-6.4 ± 0.8 (4)	-24.0 ± 0.1					
	1	24	-6.0	-23.9		6.4	3.1	9.2	+42.8
	2	10	-6.5	-24.0		6.8	3.4	9.9	+45.5
PH15.2_ LV5HS_	FIA		-27.4 ± 0.0 (2)	14.7 ± 0.3 (2)	260.6 ± 4.6				
	2	22	-27.4 ^a	14.5	268.2	28.0	9.8	35.9	+28.4
	3	20	-27.4		254.1	26.6	10.2	34.9	+31.2
	6	12	-27.4		260.6 ^a	27.2	10.0	35.3	+29.7
	8	10	-27.4 ^a		259.4	27.1	10.0	35.3	+30.3
	9	11	-27.4 ^a		261.2	27.3	10.0	35.4	+29.7
	10	10	-27.4 ^a		261.9	27.3	10.0	35.5	+29.9
	11	8	-27.4 ^a		258.6	27.0	10.1	35.2	+30.3

Table 5. Comparison between LA-ICPMS element quantification using NaCl abs. obtained from observation of two phase melting during microthermometry (left) and element quantification based on NaCl eq. determined from last halite melting combined with additional salt correction for K/Na > 0.1 (Heinrich et al. 1992, 2003) (right). (abbr.: n.i. =

not included due to insufficient signal detection (SILLS quantification resulting in concentration above the 3σ value but without a visible peak justifying the element quantification); MT = results from microthermometry; LA = results from laser ablation ICPMS; LOD = limit of detection).

FIA- Sample	FI	Value (ppm)								Value (ppm)						
		Na	K	Ca (MT)	Ca (LA)	Mn	Fe	Cs	Pb	Na	K	Ca	Mn	Fe	Cs	Pb
		Internal standard: NaCl abs. (Steele-MacInnis et al., 2011)								Internal standard: NaCl eq. (Bodnar + Vityk, 1994)						
PH15.2_ LV5HS_2	2	109800	32400	35300	27100	849	6160	193	861	127200	37500	31400	983	7130	224	997
	3	104600	26700	36700	n.i.	572	2795	149	2120	125300	32000	n.i.	685	3350	179	2540
	6	106800	14800	36100	n.i.	932	14200	91	1820	132000	18300	n.i.	1150	17500	113	2250
	8	106800	43800	36200	n.i.	2530	67500	65	1370	120400	49300	n.i.	2850	76100	74	1550
	9	107600	12400	36000	n.i.	775	16800	83	1300	133500	15400	n.i.	961	20900	103	1610
	10	107600	21400	36000	n.i.	899	19700	77	1250	130000	25800	n.i	1100	23800	93	1510
	11	106100	12200	36300	<82700	127	3160	44	779	132700	15300	<103400	159	3960	55	974
										Deviation in %						
	2	Deviation when NaCl eq. instead of NaCl abs. is used								+15.8	+15.8	+15.8	+15.8	+15.8	+15.8	+15.8
	3	as internal standard for element quantification and salt								+19.8	+19.8		+19.8	+19.8	+19.8	+19.8
	6	correction for K/Na > 0.1 is applied (Heinrich et al. 2003):								+23.6	+23.6		+23.6	+23.6	+23.6	+23.6
	8									+12.7	+12.7		+12.7	+12.7	+12.7	+12.7
	9									+24.1	+24.1		+24.1	+24.1	+24.1	+24.1
	10									+14.3	+14.3		+14.3	+14.3	+14.3	+14.3
	11									+19.8	+19.8		+19.8	+19.8	+19.8	+19.8
	Average									+20.3	+20.3		+20.3	+20.3	+20.3	+20.3

3.4 Independent Ca analysis by LA-ICPMS

In principle, the Ca/(Na+Ca) ratio can be independently measured by microthermometry as well as LA-ICPMS. However, the quantification of Ca by LA-ICPMS is imprecise because of the high background on mass ^{40}Ca and ^{42}Ca caused by the Argon plasma, limiting signal/noise ratio especially when analysing smaller FI (Fig 5). The alternative isotope ^{44}Ca overlaps with $^{28}\text{Si}^{16}\text{O}$, which may cause systematic errors that we have not yet explored. Figure 6 illustrates the scatter among individual FI from the same FIA, showing that CaCl_2 and NaCl concentrations can be more precisely determined by careful microthermometry than by LA-ICPMS. Figure 6 and Table 3 also show that due to the high background on mass 42, only 17 FI in 6 assemblages (from a total 45 FI in 10 assemblages measured with microthermometry) allowed Ca quantification using significant LA-ICPMS signals on mass ^{42}Ca . Thus, almost 2/3 of the inclusions analysed in this study would not have shown detectable Ca concentrations by LA-ICPMS, even though microthermometry clearly show Ca to be a major component. Nevertheless, among those FI where Ca was detected by LA-ICPMS, most of the Ca concentrations computed from the small ^{42}Ca signal are consistent with the more precise Ca concentration determined by microthermometry, with random deviations of mostly less than 10% (Fig. 6 and Table 3).

Figure 5. Ca/Na ratios of single fluid inclusions for six FIA determined by microthermometry show minimal variation within one assemblage, compared to ratios determined by LA-ICPMS. Open symbols indicate FI within an assemblage where microthermometry measurements required one average phase melting temperature (either ice, hydrohalite or halite) of the other inclusions in the same FIA to determine the inclusions salinity. All other symbols represent inclusions for which both melting temperatures were observed and measured directly.

Figure 6. Transient LA-ICPMS signal illustrating the signal for selected elements in counts per second (cps) versus time, and the separation of this time-resolved signal into its component parts (background, host, inclusion). Note the relatively poor ^{42}Ca /background intensity ratio obtained by LA-ICPMS due to the low elemental abundance of ^{42}Ca (0.67%).

4. Conclusion

Microthermometric measurement of two phase transitions allows absolute CaCl_2 and NaCl quantification in Ca - Na -dominated brine inclusions. This approach is applicable to obtaining Na concentration as internal standard for LA-ICPMS quantification, irrespective of the host mineral, i.e., quartz or a Ca -rich minerals like fluorite or carbonate where the host background makes LA-ICPMS measurement of Ca impossible. Our tests showed that observed ranges of phase melting temperatures are small within petrographically well-defined fluid inclusion assemblages, resulting in a narrow $\text{Ca}/(\text{Ca}+\text{Na})$ range. Therefore, even one or a few complete microthermometry data sets comprising measurement of the two last-melting phases (hydrohalite and either ice or halite), and applying these results as internal standard to all inclusions of an assemblage, will generally be a significant improvement compared with simply using wt% NaCl eq. as an internal standard for LA-ICPMS quantification of sodic-calcic brines. Given that Ca is difficult to analyse by LA-ICPMS due to high background and/or low abundance sensitivity on all masses of Ca , careful microthermometry and application of phase relations in the ternary H_2O - NaCl - CaCl_2 system is superior to any empirical correction for additional salt components in analyzing fluid inclusions of sodic-calcic brines.

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