

Synthetic fluid inclusions in natural quartz. IV. Chemical analyses of fluid inclusions by SEM/EDA: Evaluation of method

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Abstract—The compositions of individual synthetic fluid inclusions in the systems NaCl-KCl, NaCl-CaCl₂ and NaCl-KCl-CaCl₂ have been semi-quantitatively determined by energy dispersive analysis of precipitates produced during thermal decrepitation. Inclusions containing known mixtures of 20 wt.% total salinity were synthesized by healing fractures in natural quartz at 600–700°C and 5–7 kbars for 7–10 days. The two-phase, daughter-free inclusions homogenized at 170–250°C, began to decrepitate after about 100° of overheating and by 360–420°C a significant number of decrepitates had formed on the polished surface. Peak heights generated by EDA (raster mode) of these decrepitates were standardized using both single and mixed salt standards evaporated to dryness in a vacuum. Although the mixed salt standards better approximated the decrepitate compositions, difficulties were encountered in producing micron-scale homogeneity and the single salts yielded more reliable results.

Eight different solutions of 20–23 wt.% total salinity were run and in all the samples the average compositions of 10–20 discrete, single inclusion decrepitates fell within 6 wt.% (0.2 to 5.2) of the actual composition, suggesting that the decrepitates were chemically representative of their precursor inclusions. However, not all decrepitates analyzed provided similarly accurate results. Electron mapping revealed that fracture-aligned decrepitates were often chemically inhomogeneous and thus had to be avoided. A sample decrepitated at 500°C yielded spurious results suggesting that chloride volatility may become a significant problem when temperatures in excess of 450°C are required for decrepitation. Decrepitates with diameters between 10 and 30 μm yielded more consistent and accurate results than smaller or larger decrepitates on the same samples.

INTRODUCTION

ALTHOUGH FLUID INCLUSIONS are used routinely to determine the temperature and total salinity attending mineral formation, techniques for obtaining the major element composition of these tiny samples of fluid are limited, both in accuracy and scope, and remain generally untested (ROEDDER, 1984). EADINGTON (1974) proposed that qualitative, and in some cases semi-quantitative, compositional data could be obtained by energy dispersive analysis (EDA) of salt residues, here called decrepitates, left on cleavage surfaces after evaporation of inclusion fluids. Modifications of this technique have been employed subsequently to obtain semi-quantitative inclusion compositions in Australian unconformity uranium ores (YMPA and FUJIKAWA, 1980), silver-rich quartz veins of the Guadalcazar stock in central Mexico (CHRYSOULIS and WILKINSON, 1983), and Mississippi Valley-type ores of East Tennessee and Pine Point (HAYNES and KESLER, 1987). In this study, we have evaluated the accuracy and precision of the technique, as well as its limitations, by analyzing decrepitates produced from synthetic inclusions of known composition grown in natural quartz using the method of STERNER and BODNAR (1984).

PREPARATION AND ANALYSIS PROCEDURE

The synthetic fluid inclusions used in this study were produced by healing fractures in inclusion-free Brazilian quartz crystals at elevated temperature and pressure in the presence of various Na-Ca-K chloride brines. After fracturing the quartz by thermal shock, the cylindrical cores were sealed in noble-metal capsules along with the desired fluid

(STERNER and BODNAR, 1984). To insure that the inclusions would homogenize below 250°C, and thus decrepitate around 350°C (a temperature similar to those required in Mississippi Valley-type settings; HAYNES and KESLER, 1987), the fluid-filled fractures were reheated at temperatures of 600–700°C and pressures of 5–6 kbars (Fig. 1). Under these conditions the quartz fractures rehealed in 7–10 days.

The cores were quenched and 1 mm thick wafers cut and doubly polished. Prior to thermal decrepitation and SEM/EDA, the inclusions were subjected to traditional heating/freezing runs using a Fluid Inc. adapted USGS gas-flow heating/freezing stage to ensure that the inclusions in each wafer had homogeneous filling and freezing point depression temperatures.

Decrepitation was performed in the fluid inclusion stage at temperatures between 360° and 420°C (Table 1). Slightly more than 100° of heating above the homogenization temperature was required to initiate decrepitation. Fluids released during decrepitation travelled to the surface along fractures where salt precipitates (decrepitates) were deposited either in discrete mounds of presumed single inclusion origin (Fig. 2A), or in linear trails where the rehealed fractures breached the polished surface (Fig. 2B). As discussed below, the fracture-aligned decrepitates were often chemically inhomogeneous and did not yield results as reliable as the discrete single inclusion decrepitates. The decrepitated wafers were carbon coated and subjected to EDA using a JSM-U3 (JEOL) scanning electron microscope. All analyses were conducted over rastered areas covering most of the decrepitate surface. In addition to "averaging out" chemical inhomogeneities in the decrepitates and adverse effects of irregular topography, the use of rastered areas diminished the potential for differential element volatility under the electron beam. Working with precipitates from fluid microdroplets similar to those analyzed in this study, MORGAN and DAVIES (1982) and ROINEL (1975) established that element volatility is a function of beam current density and not total integrated dose. MORGAN and DAVIES (1982) further demonstrated that the elements present in this study (Na, Ca, K, and Cl) would not volatilize until beam current densities exceeded 0.5 nanoamps/μm². By employing the raster technique and maintaining a beam current of 10 nanoamps, beam current densities in this study never exceeded 0.4 nanoamps/μm² and normally ranged from 0.05 to 0.2 nanoamps/μm². Instrument settings and analytical conditions are summarized in Fig. 3.

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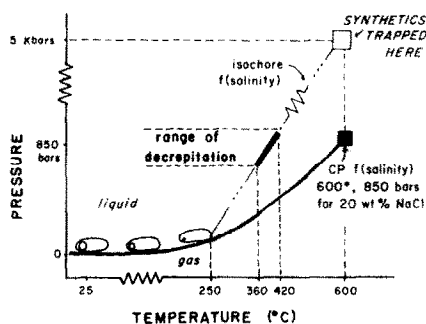


FIG. 1. Schematic phase diagram for a 20 wt.% salinity solution. The formation conditions, isochore, homogenization temperature and range of decrepitation temperatures for the synthetic inclusions are depicted.

Peak minus background heights (see below) recorded from 100 seconds of analysis (Fig. 3) were standardized and converted to wt.% chloride salts using one of two methods:

1. *Single salt standards.* Microdroplets containing each of the single salts (NaCl, KCl, CaCl₂) were placed on quartz and evaporated to dryness in a vacuum. Cation/Cl ratios obtained by energy dispersive analysis of these single salt precipitates (termed standardization factors) were used to standardize the decrepitate analyses and an interactive BASIC program converted elemental counts to wt.% chloride salts. While this technique did not permit ZAF corrections to be evaluated rigorously, it did bypass the problem of making homogeneous mixed salt standards.

2. *Mixed salt standards.* Mixed salt standards of variable composition were prepared in a manner similar to the single salts, and subjected to energy dispersive analysis with variable overlap of the matrix quartz. The resulting scans were stored in computer memory. Subsequent to each unknown analysis, a KEVEX matching standard program was accessed. The program compared the EDA scan of the unknown to each stored standard scan, selected the closest Chi-square match, and used it to standardize the analysis of the unknown. As with the single salt method, results were converted to wt.% chloride salts.

RESULTS OF DECREPITATE ANALYSES

The average compositions obtained from 15 to 20 decrepitates from each of the 6 two-component runs varied from

the actual composition by 0.2 to 5.2 wt.% (Table 1, Fig. 4) when single salts were used as standards. Standard deviations ranged from 4.7 to 9.4. Repeat analyses of the same decrepitate seldom varied more than 2 wt.%. If these results are reported in terms of modes directly from the histograms of Fig. 4, that is with 0.05 weight fraction intervals, then the actual value is included in the mode of 5 of the 6 samples.

The first attempt with the three-component inclusions, also the first attempt overall, was not as successful (Fig. 5A, Table 1). Many of the decrepitates used in this effort had formed along fractures (Fig. 2B) and it is believed that these scattered and spurious results resulted from chemical inhomogeneities which developed during decrepitate formation (discussed below). In the second attempt with these samples, and all efforts with the other samples, only decrepitates of presumed single inclusion origin (as determined by their size and morphology) were analyzed. These results were much better (Fig. 5B), and similar in accuracy and precision to those from the 6 two-component samples.

The majority of the decrepitate analyses showed excellent electrical charge balance. To check for charge balance, the products of the counts registered, the standardization factor and the charge of each of the cations present were summed and set equal to the Cl count recorded. If the cation total exceeded that of Cl, the decrepitate showed a net chlorine deficiency; analyses where the Cl count was greater were termed cation deficient. Analyses with deficiencies (chlorine or cation) of less than 6% were considered good, while a charge imbalance of between 6 and 12% was accepted as fair. Those decrepitates yielding deficiencies in excess of 12% were considered poor and were rejected. Less than 10% of the decrepitate analyses performed in this study had to be rejected due to electrical charge imbalance (Fig. 6).

Mixed salt standards

Theoretically, mixed salt standards with compositions similar to the unknown would make preferable standards, but the results of four samples analyzed using mixed salt

Table 1. Results of decrepitate analyses from synthetic inclusions. Compositions are reported in weight percent.

Sample Number	Decr. Temp. °C	Anal. Date	# of Obs.	\bar{X} : Average of measured decrepitates			Actual Composition			Total Sal.	Actual - \bar{X}			Std. Dev.
				NaCl	KCl	CaCl ₂	NaCl	KCl	CaCl ₂		NaCl	KCl	CaCl ₂	
NK1	360	4/85	15	69.8	30.2	----	75.0	25.0	----	20.0	5.2	-5.2	----	7.6
NK2	360	4/85	17	44.9	55.1	----	50.0	50.0	----	20.0	5.1	-5.1	----	4.9
NK3	360	5/85	19	24.8	75.2	----	25.0	75.0	----	20.0	0.2	-0.2	----	5.2
NC1	375	1/85	20	43.6	----	56.4	40.0	----	60.0	23.2	-3.6	----	3.6	9.4
NC2	400	12/84	15	64.7	----	35.3	59.6	----	40.4	22.5	-5.1	----	5.1	7.9
NC3	360	1/85	15	86.5	----	14.4	83.3	----	16.7	21.6	-3.2	----	3.2	4.7
NCK1(1st) ^b	420	9/84	13	31.3	19.7	49.0	45.9	13.1	41.0	21.8	-6.6	-8.0	8.3	12.3
NCK2(1st) ^b	420	9/84	14	70.9	13.8	15.3	55.1	11.5	33.5	21.6	-15.8	-2.3	18.2	16.9
NCK1(2nd)	420	5/85	13	42.1	12.4	45.6	45.9	13.1	41.0	21.8	3.8	0.7	-4.5	6.0
NCK2(2nd)	420	5/85	10	55.6	15.7	28.7	55.1	11.5	33.5	21.6	-0.5	-4.2	4.7	5.7
NC4 ^a	380	1/85	14	69.9	----	30.1	48.9	----	51.1	11.3	-21.0	----	21.0	10.1
NK2(500)	500	5/85	9	35.4	64.6	----	50.0	50.0	----	20.0	14.6	-14.6	----	10.4
NC1(mix)	375	1/85	12	31.2	----	68.8	40.0	----	60.0	23.2	8.8	----	-8.8	7.1
NC3(mix)	400	12/84	18	81.1	----	18.9	83.3	----	16.7	21.6	2.2	----	-2.2	6.5
NK1(mix)	360	4/85	12	67.3	32.7	----	75.0	25.0	----	20.0	7.7	-7.7	----	12.5
NK2(mix)	360	4/85	16	35.6	64.4	----	50.0	50.0	----	20.0	14.4	-14.4	----	9.0

^a poor results believed to result from lower salinity and hence smaller size of decrepitate (see text)

^b poor results believed to result from lack of understanding of size, fracture-hosted decrepitate inhomogeneity and carbon coating limitations (see text)

(mix)- results obtained using mixed salt standards (see text)

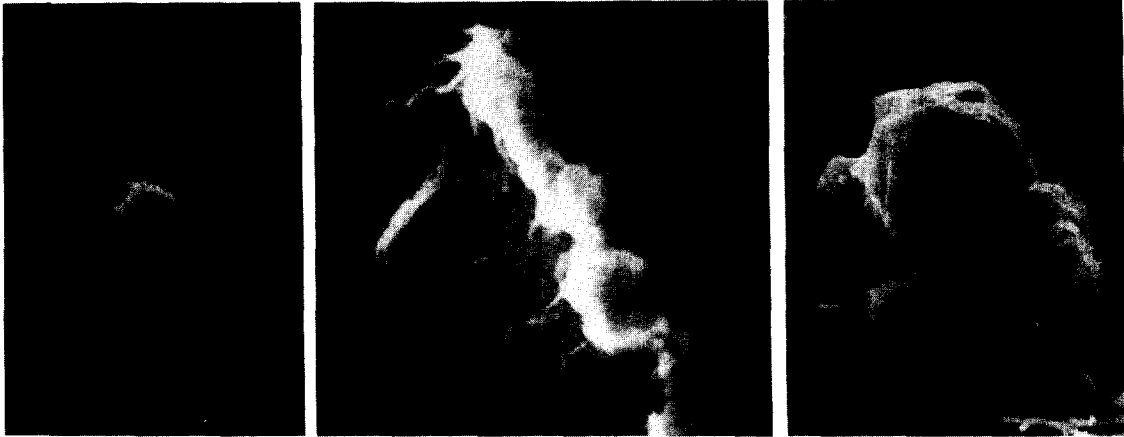


FIG. 2. Scanning electron photomicrographs of fluid inclusion-derived decrepitate salts. Scale bars are 10 μm long. A. Discrete decrepitate on NCK2 of presumed single inclusion origin. B. Fracture-aligned linear decrepitate occurring where a plane of inclusions breached the surface. Decrepitates of this character are often inhomogeneous (see electron maps in Fig. 9) and do not make good targets for analysis. C. Non-homogeneous solid residue produced when sample NC2 was left in a desiccator for two weeks between decrepitation and analysis. The crystals farthest from the edifice are pure NaCl, the mass behind them and the hair-like material consists of mixed Na-Ca chloride salts.

standards (Fig. 7) show poorer accuracy and precision than their counterparts using single salt standards. The compositions determined by the mixed salt method are strongly dependent upon which standard the KEVEX matching program selected as the best Chi-square fit for that analysis. In each of the samples the "best-fit" standards do not differ in cation chemistry, but rather in the extent of overlap with the matrix quartz, and therefore in the intensities of the cation and chlorine peaks. These results suggest that problems in creating homogeneous mixed salt standards are (at present) greater than those associated with single salt standards. Consequently, single salt standards were used throughout this study.

Peak heights versus peak areas

Nineteen decrepitates from two samples were analyzed using both peak heights and peak areas (Table 2). Compositions obtained using peak minus background heights, measured directly from the scan, and those obtained using peak area programs were statistically indistinguishable at a 95% con-

fidence interval in both samples. Neither the accuracy nor the precision was improved by incorporating the more rigorous peak area determinations. These results are thought to reflect the semi-quantitative nature of the analysis.

Homogeneity

To test for homogeneity, selected decrepitates from NC1, NK2, NCK1, and NCK2 were divided into quadrants, each of which was analyzed under the same conditions as the total decrepitate. In all seven decrepitates subjected to these multiple analyses, variations among the analyses were small, in the order of 1–3 wt.%, and probably reflected the precision of the method rather than chemical inhomogeneities (Table 3).

Electron mapping was also utilized routinely as a qualitative test of the homogeneity of decrepitates. Most regularly shaped, presumably single inclusion-derived decrepitates yielded homogeneous electron map patterns (Fig. 8). Those that did not pass this qualitative test were not analyzed.

Decrepitates that formed along major fractures where planes of secondary inclusions broke to the surface often did not show chemical homogeneity (Fig. 9). Optical observations of the decrepitation process may help to explain this heterogeneity. Fracture-controlled decrepitate formation typically required several seconds as an entire plane of inclusions leaked to the surface and precipitated its salts, whereas individual inclusion decrepitations were seemingly instantaneous events. Rapid evaporation and precipitation, which characterized decrepitation of individual inclusions, may be essential in preventing differentiation and redistribution of elements within the solid residue and thus in preserving chemical homogeneity in the decrepitate (at least at the scale of this analytical method). Compositional data obtained from fracture-aligned decrepitates must be interpreted with caution. The poor results from the initial NCK samples are believed to have resulted from this problem as fracture-aligned decrepitates were included in these early efforts.

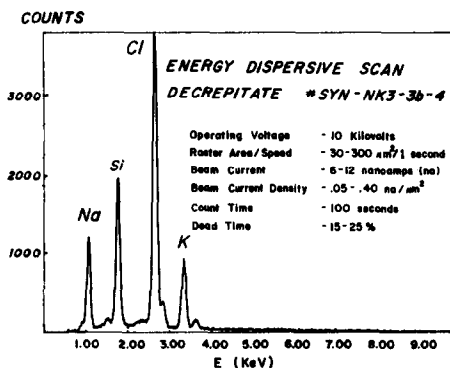


FIG. 3. Energy dispersive scan from a typical Na-K chloride decrepitate on synthetic quartz and the operating conditions under which the analysis was undertaken.

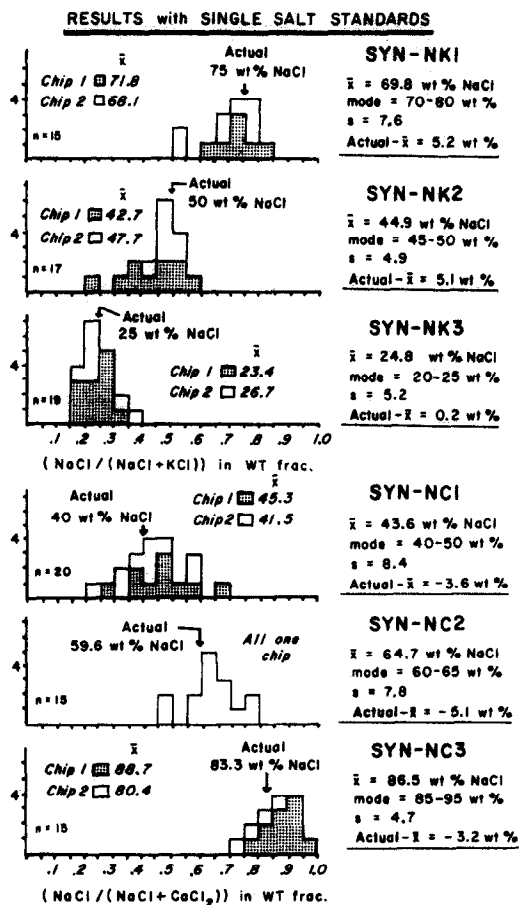


FIG. 4. The results of decrepitate analyses from the six two-component samples (NaCl-KCl and NaCl-CaCl₂) and their actual compositions. These results, all obtained using single salt standards, are tabulated in Table 1. (Abbr.: \bar{x} = average of decrepitate analyses, s = standard deviation).

Non-homogeneous salts are also produced (either through CaCl₂ deliquescence or NaCl and/or KCl creep) when samples are left in a desiccator for several days between decrepitation

and analysis (Fig. 2C). Inhomogeneity of this type can be avoided by analyzing samples with a few hours of decrepitation.

LIMITATIONS

Decrepitate size, inclusion size and inclusion salinity

The size of any single-inclusion decrepitate is a function of the size of the parent inclusion and the amount of dissolved non-volatile solid, in this case, the total salinity. Expressed volumetrically, the volume fraction of salt in an inclusion times the volume of the inclusion is equal to the volume of solid residue produced on decrepitation plus the volume of solute lost through vaporization and spatter. Modelling the parent inclusions as spheres and the decrepitates as hemi-ellipsoids, with heights equal to one-half their radii (HAYNES and KESLER, 1987) and assuming that the volume of solute lost is insignificant (discussed below), then the relationship is defined by:

$$\frac{ws}{100} \times \frac{4\pi r_i^3}{3} = \frac{\pi p r_d^3}{3} \tag{1}$$

or

$$wsr_i^3 = pr_d^3 \tag{2}$$

where *w* is a factor converting wt.% salinity (*s*) to volume %, *r_i* is the inclusion radius, *r_d* is the decrepitate radius and *p* is a porosity factor for the decrepitate. The salinity term (*ws*) is converted to volume fraction by dividing by 100. To further simplify estimations of decrepitate volumes, salinities have been expressed in NaCl wt.% equivalents (thus, *w* = 18 grams H₂O per mole/58.5 grams NaCl per mole = 0.308) and *p* is set at 0.85 based on an estimation of 15% porosity for the decrepitates by high magnification scanning electron microscopy. The relationship between inclusion size, inclusion salinity, and decrepitate size reduces to:

$$0.0145sr_i^3 = r_d^3 \tag{3}$$

an expression that can be illustrated graphically for the full range of inclusion sizes and salinities pertinent to this study

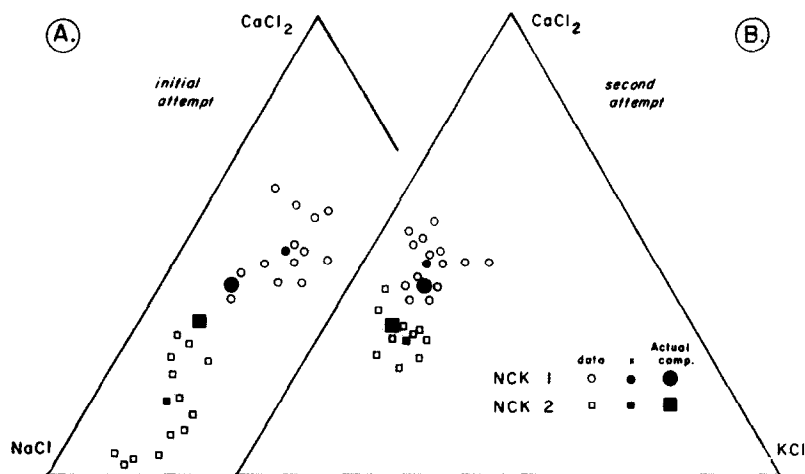


FIG. 5. The results of two attempts with the three-component samples (NaCl-KCl-CaCl₂) plotted in wt.%. These results are tabulated in Table 1.

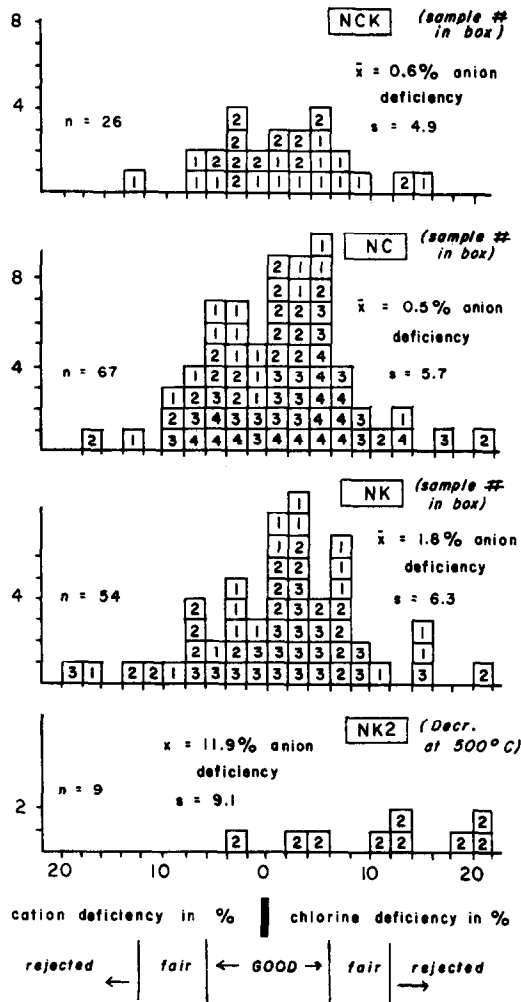


FIG. 6. Calculations of electrical charge balance in the decrepitate analyses. The top three histograms record the results of all samples (with their numbers) decrepitated below 420°C. The bottom histogram shows the unbalanced, chloride-deficient, analyses recorded when sample NK2 was reheated to 500°C.

(Fig. 10). Given the salinity of the synthetic inclusions (20–23 wt.%) and their typical size (5–40 μm) the nomogram indicates that decrepitates from single inclusions should range from 3–25 μm in diameter. With the exception of the solid residues from rare, isolated larger inclusions, decrepitates larger than 25 μm likely represent the solute fractions of more than one inclusion.

To investigate the limitations that decrepitate size places on the quality of an analysis, and thus the mutual restrictions on inclusion size and salinity as defined by Eqn. (3), the compositions determined from decrepitates on two of the samples have been plotted against their diameters (Fig. 11). In both cases, the data indicate an optimum decrepitate diameter in the range 8–30 μm. Smaller decrepitates appear to approach the limit of the raster mode method of analysis as both the beam current density and matrix overlap increase geometrically with decreasing raster size. The presence of an upper size limit on accurate analysis is less easily explained, except

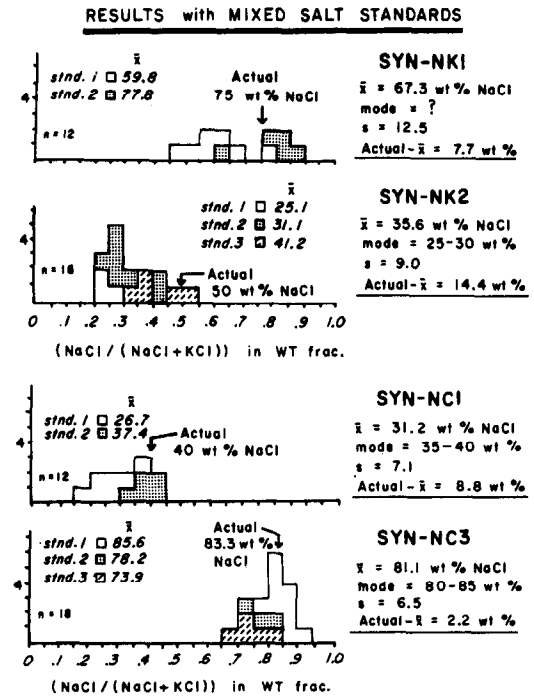


FIG. 7. The results obtained when mixed salts were used as standards and the actual compositions. The different standards (stdn.) shown in each histogram represent the standards selected by the KEVEX matching standard program during analysis (see text). (Abbr.: \bar{x} = average of decrepitate analyses, s = standard deviation).

that electron mapping reveals that these larger decrepitates are often chemically inhomogeneous. Because decrepitates greater than about 30 μm in diameter are likely the product of more than one inclusion it is possible that this inhomogeneity originates from processes of element redistribution related to multiple decrepitation events at the same site.

In a further test, inclusions containing a NaCl-CaCl₂ solution of 11.3 wt.% total salinity were grown, decrepitated and analyzed (Table 1, Fig. 12A). The average composition of 14 decrepitates from two chips was 69.9 wt.% NaCl, 21.0 wt.% and more than two standard deviations greater than the actual concentration of 48.9 wt.% NaCl. As the nomogram predicted, the decrepitates were small; 12 of the 14 analyzed

Table 2. Comparison of results using peak heights and peak areas.

SYN-NK3 (Chip #1)			SYN-NK3 (Chip # 1)		
by Areas	by Heights	difference	by Areas	by Heights	difference
19.1	19.4	-0.3	15.5	12.0	+3.5
32.7	38.7	-6.0	18.2	17.6	+0.6
17.3	17.3	0.0	10.5	12.4	-1.9
19.7	22.3	-2.6	13.4	16.4	-3.0
27.9	17.6	+10.3	16.0	14.1	+1.9
24.5	20.2	+4.3	17.2	16.5	+0.7
24.9	24.2	+0.7	12.4	13.2	-0.8
28.9	30.4	-1.5	15.9	15.3	+0.6
23.4	21.8	+1.6			
27.0	23.9	+3.1			
23.7	21.5	+2.2			
24.4	23.4	3.0 ^{a,b}	AUG. 14.9	14.7	1.6 ^a

^a Average differences calculated from absolute values of individual differences
^b 2.2 if #5 (10.3) is excluded

Table 3. Results of homogeneity tests on 7 decrepitates

Area of Analysis ^a	SYN-NC1 ^b		SYN-NK2 ^c		SYN-NCK1 ^b				SYN-NCK2 ^b	
	# 1 NaCl	# 2 NaCl	# 1 NaCl	# 2 NaCl	Number 1 NaCl	KCl	Number 2 NaCl	KCl	NaCl	KCl
Quad. 1	38.4	48.6	43.1	50.4	39.6	11.3	53.2	12.2	62.2	12.5
Quad. 2	39.1	49.3	42.7	47.6	38.3	10.7	48.8	12.6	64.9	10.4
Quad. 3	40.7	52.2	46.1	47.3	42.8	10.3	51.7	10.9	63.6	10.8
Quad. 4	38.6	50.6	43.8	50.5	40.3	10.0	51.6	13.4	62.9	11.3
Whole	39.7	50.3	43.6	48.2	40.1	11.4	50.6	12.4	64.5	10.6

data are reported in wt. %

a Quad 1 to 4 refers to analyses of each quarter of the decrepitate
Whole refers to an analysis of the entire decrepitate

b Remainder is CaCl₂
c Remainder is KCl

had diameters less than 15 μm . It is suspected that the poor results from this sample are related to the small decrepitate size, in this case a function of the lower salinity of the inclusion fluid.

Decrepitation temperature

Upon decrepitation, inclusion contents are separated into volatile and non-volatile fractions. Clearly, estimating inclusion chemistry by SEM/EDA of the solid non-volatile fraction involves the tacit assumption that none of the salt component is lost during decrepitation, either through vaporization or spattering. Owing to the large difference in volatility among the cation chlorides of interest, any significant amount of

vaporization would almost certainly lead to fractionation between the vapor and solid products, making analysis of either fraction futile (ROEDDER, 1984). Insofar as ICP atomic emission spectrometry of the vaporized product of high temperature (>500°C) decrepitation has been applied to inclusion analysis (ALDERTON *et al.*, 1982; THOMPSON *et al.*, 1980), it is imperative that the conditions leading to partial elemental volatility be evaluated. First and foremost of these is the temperature of decrepitation.

All of the successful analyses in this study (Table 1) were conducted on samples where decrepitation was performed at temperatures at or below 420°C. To investigate the effects of inclusion decrepitation at higher temperature, previously analyzed chip NK2 was cleaned and heated to 500°C. Inclu-

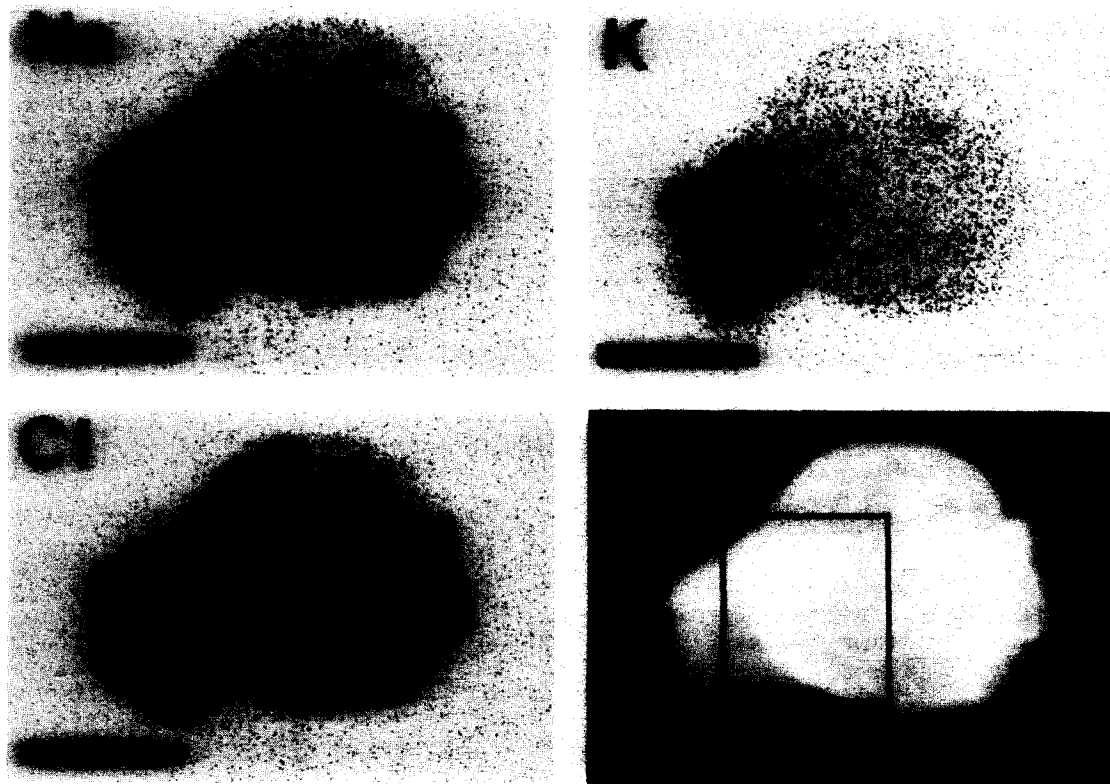


FIG. 8. Electron maps of Na, K, and Cl from a decrepitate on NK1 and a photomicrograph of that decrepitate. Na and Cl maps were taken using a 128 second collection scan, a 256 second scan was used for K. Scale bar is 10 μm .

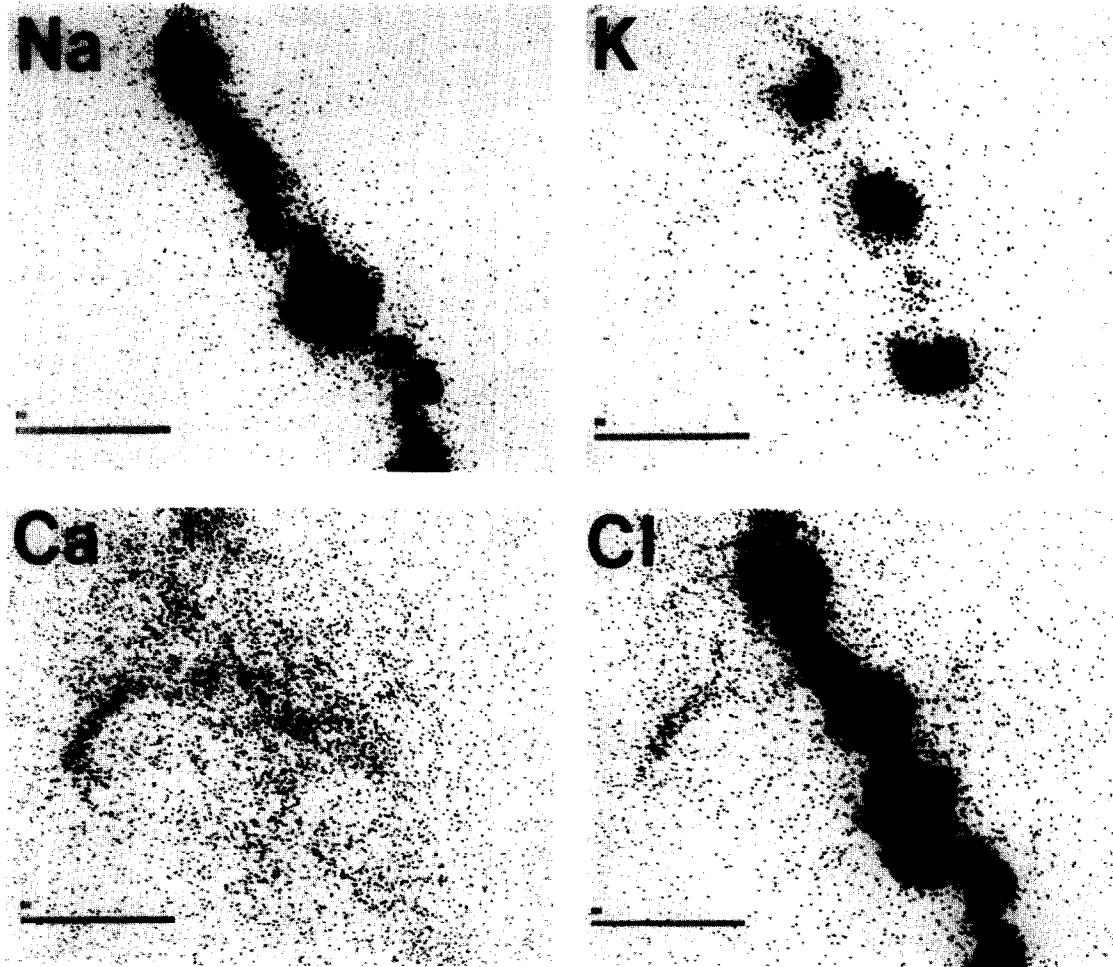


FIG. 9. Electron maps of Na, Ca, K, and Cl from the fracture-aligned decrepitate depicted in Fig. 2B. Na and K are localized along the fracture and discrete halite and sylvite crystals can be discerned. Most of the Ca lies peripheral to the main mass of Na-K chloride along the fracture. All scans took 128 seconds. Scale bar is 10 μm .

sions that survived the earlier heating to 360°C decrepitated at this elevated temperature. The nine decrepitates analyzed from this second heating showed a marked deficiency in chlorine (Fig. 6) and were significantly depleted in NaCl as recorded by their NaCl/(NaCl + KCl) ratios (Fig. 12B). These results suggest that differences in the volatility of the various solutes in the inclusion fluids may be a problem when decrepitation temperatures in excess of 400°C are employed, and the assumption that the fraction of solute component lost through vaporization and/or spatter is volumetrically insignificant may be in error under these conditions. Implicit in this evaluation is the possibility that ICP methods for inclusion analysis may require sufficiently high decrepitation temperatures such that volatilization is complete and no non-volatile salt precipitate is formed.

Major element composition (additional aqueous and volatile components)

Only inclusions containing Na, K, and Ca chloride salts in H₂O have been tested in this study. The effects of additional

components (even in small quantities) on decrepitate morphology and homogeneity and solute volatility is unknown. QUAN *et al.* (1984, 1987) found that Fe present in magma-derived fluid inclusions associated with British Columbia porphyry copper systems was localized in the margins of thermally-produced decrepitates making quantitative analysis very difficult. Of equal concern are the possible effects that additional volatile phase, CO₂ or H₂S, might have on decrepitate chemistry through reaction with solute components at the elevated temperatures of decrepitation (PISUTHA-ARNOLD and OHMOTO 1984; WALSH *et al.*, 1984).

Minor and trace elements

The synthetic inclusions prepared for this study contained only major element chloride salts, and as such they do not provide an accurate appraisal of the detection limits of decrepitate analysis. Inclusion fluids in sample NCK2 contained 13,000 ppm K, the smallest amount of any cation in any of the samples; the K peak was clearly evident, and quantifiable, in all analyses from this sample suggesting that

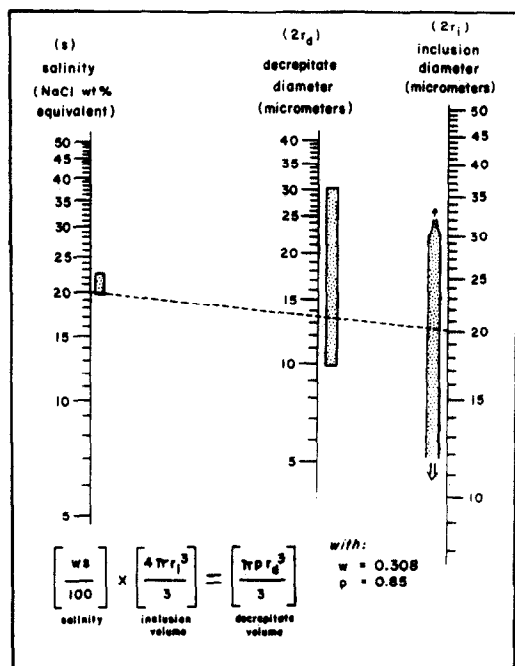


FIG. 10. Nomogram relating inclusion size, NaCl wt.% equivalent salinity, and decrepitate diameter. The range of salinities for which successful analyses were obtained in this study, the size range of inclusions, and the range of decrepitate diameters determined to be "optimum" for analysis are depicted by the stippled boxes. The dashed line illustrates the use of the nomogram; an inclusion with a diameter of 20 μm and a salinity of 20 wt.% NaCl equivalent would be expected to yield a decrepitate with a diameter of slightly less than 13.5 μm . (Abbr.: w = weight to volume conversion factor, s = total salinity in equivalent wt.% NaCl, r_i = inclusion radius, r_d = decrepitate radius, and p = a porosity factor for the decrepitate; see text).

detection limits are significantly lower. Based on comparative efforts involving natural samples, we believe that successful semi-quantitative analysis likely requires that the element comprise at least 0.5 wt.% of the decrepitate (or 1,000 ppm in a 20 wt.% chloride solution). The noisy background inherent in EDA and enhanced by the irregular topography of the decrepitates likely precludes the detection of elements present in quantities of less than a few hundred ppm. For example, metals (Pb, Zn, Cu) present in 10–100 ppm quantities in the mineralizing basinal brines for Mississippi Valley-type ores (CARPENTER *et al.*, 1974) were not detected in decrepitates from East Tennessee and Pine Point ore-stage samples (HAYNES and KESLER, 1987).

Daughter minerals

All inclusions decrepitated and analyzed in this study contained only two phases (liquid and vapor) at room temperature. Theoretically, the presence of soluble daughter salts (halite, sylvite, etc.) should not effect the analysis adversely as long as these salts dissolve completely prior to decrepitation. On the other hand, the presence of non-soluble salts, or salts which undergo only partial dissolution prior to decrepitation, will detract from the quality of a decrepitate

analysis in that the solid daughter phase will remain in the parent inclusion and its constituent elements will be under-represented in the decrepitate. Studies involving natural samples in which daughter minerals are present should be preceded by optical observations ensuring that the daughters do dissolve before decrepitation temperatures are reached.

CONCLUSIONS

The results of analyses performed on eight samples of natural quartz containing synthetic inclusions of known compositions in the systems NaCl-KCl, NaCl-CaCl₂ and NaCl-KCl-CaCl₂ show that the compositions of moderately to highly saline fluid inclusions can be determined semi-quantitatively by SEM/EDA of the solid residue produced during thermal decrepitation. Analyses conducted using single salt standards were more accurate (averages of 10–20 decrepitates varied less than 5 wt.% from the known compositions) than those performed with theoretically superior mixed salt standards.

The study revealed several limitations that must be evaluated for each new application of the technique:

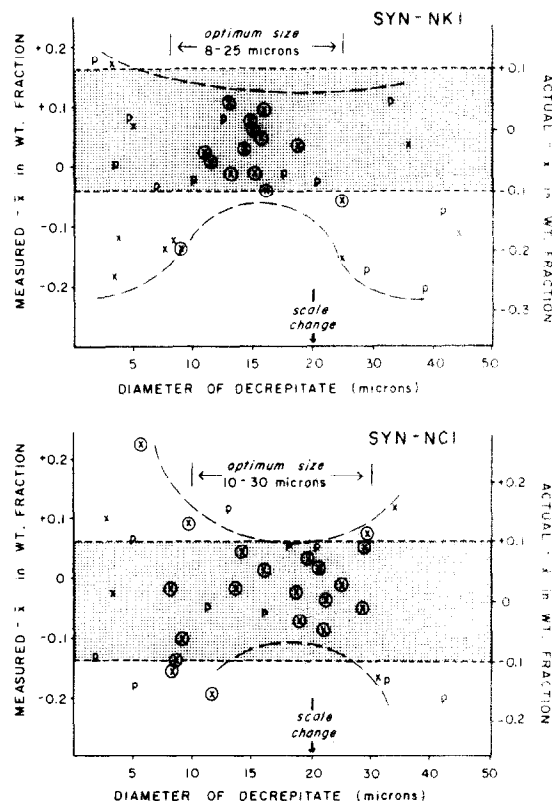


FIG. 11. Decrepitate diameter plotted against the difference between the analyses from x (left y -axis) and between the analyses and the actual composition (right y -axis) for decrepitates from samples NK1 and NC1. The hatched fields mark the region with 0.1 wt. frac. of the actual composition. (Abbr.: x = charge balanced analyses not in the optimum size range, circled x = charge balanced analyses used in Table 1 and Fig. 4, p = poorly balanced analyses (>12% imbalance between cations and chlorine)).

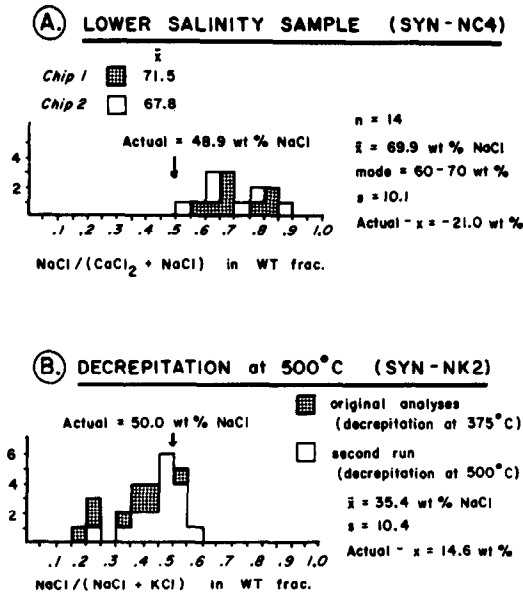


FIG 12. A. Results from NC4 containing lower salinity inclusions. B. Results from 500°C reheating decrepitation run with NK2. Data from the original analyses are also included.

1.) Chemical inhomogeneities can develop during the formation of the decrepitates. Electron mapping can be used to detect these inhomogeneities.

2.) Decrepitation must be performed at temperatures below about 450°C. Differential volatility of the various chloride salts in the inclusion introduces sizable error when higher temperatures are employed.

3.) Decrepitate size, a function of inclusion size and salinity, must be optimized. 10–30 μm diameter decrepitates yielded the best results in this study.

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