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DETERMINATION OF THE LOCAL STRUCTURE AND SPECIATION OF ZINC IN INDIVIDUAL HYPERSALINE FLUID INCLUSIONS BY MICRO-XAFS

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ABSTRACT

X-ray absorption fine structure (XAFS) spectra were obtained for the first time from metal complexes in individual fluid inclusions in quartz using the synchrotron X-ray microprobe (X26A) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Analysis of Zn *K*-edge absorption spectra obtained from hypersaline fluid inclusions in quartz indicate that the dominant complex of zinc in these inclusions at room temperature is $ZnCl_4^{2-}$, having a Zn–Cl bond length of 2.33 Å, coordination number of 4.2 atoms and a mean-square relative displacement of the atoms of 0.004 Å^2. XAFS spectra obtained from zinc chloride test solutions having a Cl/Zn ratio of 8 closely match the spectra derived from the inclusions. The presence of $ZnCl_4^{2-}$ is consistent with results of previous spectroscopic studies of zinc chloride solutions having high Cl/Zn ratios and with solubility studies of zinc compounds in chloride solutions. Our results demonstrate the potential of micro-XAFS as a tool for direct measurement of the structure of aqueous metallic species in fluid inclusions. The sensitivity of the method will improve as brighter and more focussed X-ray beams become available.

Keywords: fluid inclusion, X-ray absorption fine structure, XAFS, metalliferous brine, chlorozinc complex, local structure, synchrotron X-ray microprobe, synchrotron X-ray fluorescence.

SOMMAIRE

Des spectres d'absorption X (XAFS) de complexes métallifères dans des inclusions fluides individuelles piégées dans le quartz sont ici présentés pour la première fois; nous les avons obtenus avec une microsonde (X26A) utilisée avec une source synchrotron au National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. L'analyse des spectres de l'absorption *K* du zinc dans les inclusions fluides hypersalines dans le quartz indiquent que le complexe dominant à température ambiante serait $ZnCl_4^{2-}$, possédant une liaison Zn–Cl de 2.33 Å, une coordinence de 4.2 atomes, et un déplacement moyen relatif des atomes de 0.004 Å^2. Les spectres XAFS obtenus de solutions témoins de chlorure de zinc ayant un rapport Cl/Zn de 8 ressemblent étroitement aux spectres des inclusions. La présence de $ZnCl_4^{2-}$ concorde avec les résultats d'études spectroscopiques antérieures de solutions de chlorure de zinc ayant un rapport de Cl à Zn élevé et avec la solubilité de composés de zinc en solutions chlorurées. Nos résultats démontrent le potentiel de la technique micro-XAFS comme outil pour mesurer directement la structure d'espèces métalliques aqueuses dans les inclusions fluides. La sensibilité de la méthode augmentera avec toute amélioration dans la luminosité et la focalisation du faisceau de rayons X.

(Traduit par la Rédaction)

Mots-clés: inclusion fluide, structure fine de l'absorption X, XAFS, saumure métallifère, complexe de chlorozinc, structure locale, microsonde X à source synchrotron, fluorescence X à source synchrotron.

INTRODUCTION

It is well known that complex ions are largely responsible for metal transport in hydrothermal systems (Barnes 1979), and that the fundamental thermodynamic properties of aqueous metallic species are defined by molecular structure and bond strengths (Susak & Crerar 1985). It is, therefore, important to know the molecular properties of complex ions, over a range of geologically pertinent pressures and temperatures, in order to gain a complete understanding of the chemistry of hydrothermal ore deposition (Crerar *et al.* 1985). Although studies of the solubility of minerals have provided valuable information on the chemical controls of the behavior of metal complexes in hydrothermal fluids (Baes & Mesmer 1976, Barnes 1979, Seward 1981), there is still relatively little known about the molecular properties of aqueous metal species in natural hydrothermal systems (Brimhall & Crerar 1987).

Direct information on the structure of aqueous solutions has previously been obtained by means of techniques such as visible, infrared and ultraviolet spectroscopies (Buback 1981, Susak & Crerar 1985, Heinrich & Seward 1990), Raman scattering (Quicksall & Spiro 1966, Yamaguchi *et al.* 1989), X-ray diffraction (Magini *et al.* 1988), broadband ultrasonic spectroscopy (Kaatze & Wehrmann 1992), X-ray absorption spectroscopy (Eisenberger & Kincaid 1975, Lagarde *et al.* 1980, Apted *et al.* 1985), neutron diffraction (Neilson *et al.* 1981, Magini *et al.* 1988) and nuclear magnetic resonance (Li & Popov 1982). In most of these studies, relatively large volumes of concentrated solution were analyzed. In the present study, however, the goal is to obtain direct structural information on comparatively low concentrations of metal complexes within small volumes of solution trapped within individual natural fluid inclusions.

Providing that the chemical integrity of the original trapped fluid has not been modified by re-equilibration (*e.g.*, Qin *et a*l. 1992, Hall & Sterner 1993) or some other post-entrapment process such as necking (Roedder 1984), fluid inclusions represent actual samples of paleohydrothermal solutions. Thus the analysis of inclusions can provide direct information on the chemistry of the fluids involved in fluid-related geochemical processes such as hydrothermal deposition of ore. The relevant analytical techniques for fluid inclusion analysis have been reviewed by Roedder (1991) and, more recently, by Boiron & Dubessy (1994). The existing techniques have provided useful information on constituents such as gases, ions and hydrocarbon molecules. Raman spectroscopy has been particularly useful for the study of S and C species in fluid inclusions, but no technique has yet provided data on the structure of metallic complexes in single, unopened fluid inclusions.

In this study, we chose to use micro-scale X-ray absorption fine structure (micro-XAFS) to investigate the atomic structure surrounding metals within single fluid inclusions. It is desirable in studies of fluid inclusions to use a technique capable of analyzing individual inclusions of known or presumed origin, rather than analyzing many inclusions in a large volume of mineral, which may contain multiple generations of fluid inclusions (Roedder 1984). The potential of micro-XAFS for investigating microregions within a polished thin section was recently demonstrated by Hayakawa *et al.* (1991). Several attributes of micro-XAFS make it well suited for studies of speciation in metalliferous brines trapped in fluid inclusions: 1) it is an element-specific technique, making it ideally suited for studies on multicomponent systems, 2) it can provide direct information about interatomic distances and coordination numbers, 3) it can be used on structurally disordered systems, 4) it is sensitive to type of coordinating ion, and 5) it is a "point" analytical technique that can be used to obtain data from a single unopened fluid inclusion.

Anderson *et al.* (1993) collected data on the Sr *K*-edge XAFS from aqueous species of strontium in a single large group of synthetic inclusions in quartz by analyzing a large volume with a broad X-ray beam (>1 mm^2). In this paper, we present the first successful determination of the structure of a transition-metal complex in an individual fluid inclusion using micro-XAFS and extend the brief treatment of the preliminary results of our study presented previously (Mayanovic *et al.* 1995). Zn *K*-edge absorption spectra, obtained from unopened natural fluid inclusions in quartz, were used to determine the local structure of the dominant complex of zinc. Zn was selected in this initial study because the strong Zn$K\alpha$ fluorescence signal obtained from the aqueous fluid in the fluid inclusions, the weak attenuation of the Zn$K\alpha$ X-rays in quartz, the availability of experimental information on zinc complexes in hydrothermal fluids (Ruaya & Seward 1986, Bourcier & Barnes 1987), the availability of data on the structure of zinc complexes from direct methods such as EXAFS (Parkhurst *et al.* 1984, Dreier & Rabe 1986, Helz *et al.* 1993), X-ray diffraction (Yamaguchi *et al.* 1989), and Raman scattering (Morris *et al.* 1963), and finally, because zinc is a transition metal of economic interest.

METHODS

Preparation of fluid inclusion wafers, petrography of fluid inclusions and microthermometry

Doubly polished wafers were prepared from quartz obtained from a pegmatite dyke that intrudes granulites of the Saxon Granulite Massif, Germany. These pegmatites occur in the Grimmscher Granulite quarry, near the town of Limbach, and consist of orthoclase, quartz, biotite, lepidolite, tourmaline and cordierite

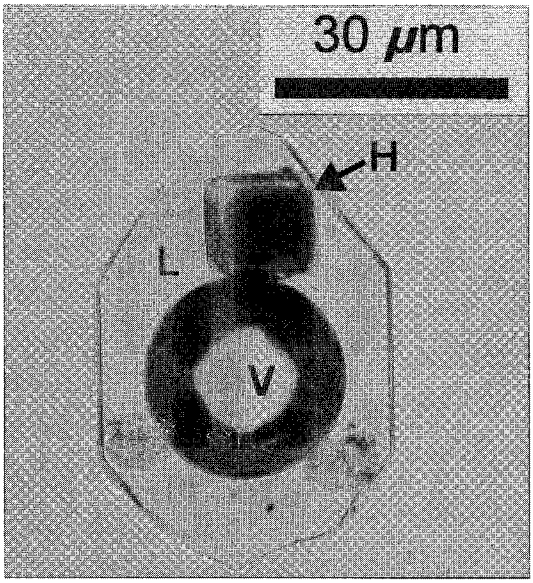

FIG. 1. Type-1 hypersaline fluid inclusion in quartz from a pegmatite in granulite-facies rocks of the Saxon Granulite Massif, Germany. At room temperature, the inclusion contains: a vapor bubble (V), a saline liquid (L), a halite daughter crystal (H), and two clusters of unidentified solid phases. The darkening of the halite crystal occurred during exposure to the X rays.

(R. Thomas, pers. comm.). The pegmatite bodies in this quarry may be related to the Mittweida monzogranite, which yields an Rb–Sr date of 350 ± 5 Ma (Haase *et al.* 1987). The polished wafers were washed with acetone in an ultrasonic bath for 20 minutes, dried, and then mounted on a pure SiO_2-glass disc with cyanoacrylate cement.

Petrographic observation revealed two types of fluid inclusions: 1) multiphase, hypersaline inclusions (Fig. 1), and 2) vapor-rich inclusions. Both types of inclusion occur as planar arrays within healed fractures and exhibit negative crystal forms that attain 110 μm in their maximum dimension. Five hypersaline fluid inclusions situated less than 20 μm from the polished surface of the mineral were targeted for analysis. At room temperature, type-1 inclusions typically contain a vapor bubble (*ca.* 30 vol.%), a saline aqueous fluid (*ca.* 55 vol.%), halite as a daughter crystal (*ca.* 10 vol.%), a high-birefringence Fe-rich daughter mineral (<3 vol.%), and about 2 vol.% of unidentified solid phases. The dimensions of individual fluid inclusions and their depths beneath the polished surface of the quartz host were accurately measured using a modified spindle stage (Anderson & Bodnar 1993) and an image analysis system.

Microthermometric analysis of fluid inclusions was performed with a Linkham THMS 600 programmable heating–freezing stage. The system was calibrated using synthetic fluid inclusions and various melting-point standards. Temperatures of liquid–vapor homogenization for type-1 inclusions range from 470 to 495°C (n = 10). Halite dissolution occurs at 216°C. Type-1 inclusions are interpreted to represent the products of a high-temperature chloride-rich brine exsolved from the granitic magma during cooling.

Preparation of test solutions

Previous investigations of fluid inclusions and experimental studies from a range of geological environments and systems suggest that Cl^- is an important ligand under hydrothermal conditions (Barnes 1979). The presence of halite as a daughter crystal in the type-1 fluid inclusions indicates that Cl^- is present in sufficient quantities to associate with the metals in the environment studied here. Thus, standard aqueous solutions of zinc chloride were prepared by preweighing reagent-grade powders of $ZnCl_2$ and NaCl. The zinc chloride was weighed under dry atmosphere conditions and dissolved in deionized, distilled water to make a 1 M $ZnCl_2$ solution. The stoichiometric ratio of Cl to Zn ions in solution was controlled by adding specific amounts of NaCl to the solution. The Cl:Zn ratio of the final solution was made equal to 8 to ensure that the dominant Zn complex at room temperature was $ZnCl_4^{2-}$ (Easteal *et al.* 1983, Giaquinta *et al.* 1983, Ruaya & Seward 1986).

The solution was prepared two hours before analysis. A pipet was used to transfer a small amount of the solution into a 0.5 mL glass reservoir. The end of a SiO_2-glass capillary tube (outer diameter 200 μm, and wall thickness 10 μm) was lowered into the solution, which was drawn up into the tube, above the solution level in the glass holder, by capillary action. The sample holder together with the capillary tube was attached to the X–Y–Z–θ mobile stage of the X-ray microprobe beam line (X26A), and a fluid-filled segment of the capillary tube was selected for analysis. The XAFS data obtained from these test solutions were needed for standardization.

X-ray-fluorescence analysis and X-ray elemental mapping of individual fluid inclusions

Synchrotron X-ray fluorescence (SXRF) spectra were obtained from ten hypersaline (type-1) inclusions using the X-ray microprobe beam line X26A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, New York, using an incident-beam spot size of 12 × 9 μm. Extremely fine slits were used to collimate the beam, and a Si(Li) detector was used to collect the fluorescence signal. The XRF spectra reveal the presence of Mn, Fe, Zn, Pb, and Br in all fluid inclusions (Fig. 2). However, many other elements are also likely to be

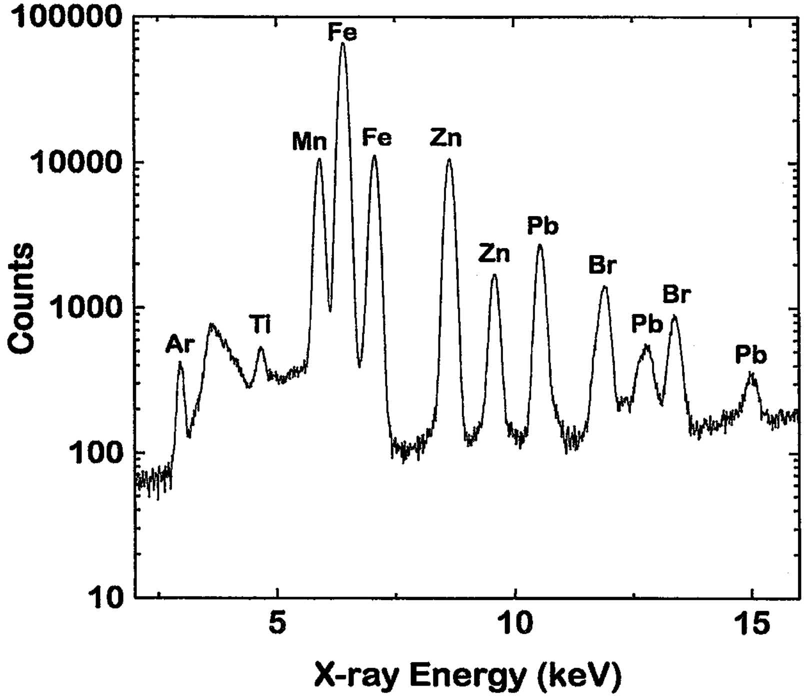

FIG. 2. Synchrotron X-ray-fluorescence (SXRF) spectrum obtained from the fluid inclusion shown in Figure 1. The spectrum reveals the presence of Mn, Fe, Zn, Pb and Br in the fluid inclusion. Ar and Ti are contributed from air and the quartz host, respectively.

present, but were not detected owing to limitations in detector sensitivities coupled with signal loss by absorption of X rays in the overlying quartz. Metalliferous brines of broadly comparable compositions have been reported in fluid inclusions from the Bingham porphyry copper deposit, Utah (Anderson *et al.* 1989), and the Mole granite, New South Wales, Australia (Heinrich & Ryan 1992, Rankin *et al.* 1992).

The presence of two or more zinc-bearing phases (aqueous or solid) within an inclusion can severely complicate the absorption spectrum. It was therefore necessary to determine whether zinc is a single- or multiple-phase constituent in the inclusions. This was accomplished by mapping the distribution of zinc in individual fluid inclusions by collecting Zn$K\alpha$ fluorescence X-ray emissions in 10-μm steps across the inclusion, in both directions in the plane perpendicular to the direction of the incident beam (Fig. 3). The volume of fluid traversed by the microbeam varies from one point in the inclusion to another, and so the intensity of the X-ray signal varies as a function of the thickness and internal structure of the inclusion.

Figures 3a and 3b respectively show variations in the intensity of the Zn and Br $K\alpha$ signals from a single fluid inclusion. Note that the experimental conditions used in this study made it possible to resolve the vapor bubble (Fig. 3). Bromine was selected for comparison because it tends to concentrate in the solution as daughter crystals precipitate. As salts precipitate in a brine, the bromine content of the solution increases significantly relative to the total dissolved solids (Valyaskho 1956). Experimental work by Braitsch & Herrmann (1963) indicates that the partition coefficient $Br_{crystals}/Br_{liquid}$ in brines is very small (0.073 to 0.16).

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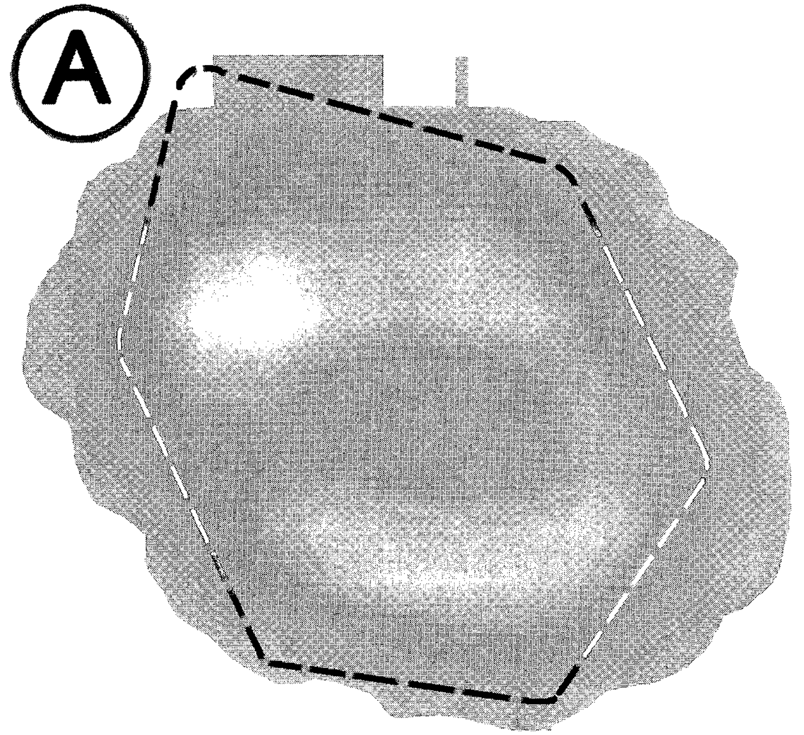
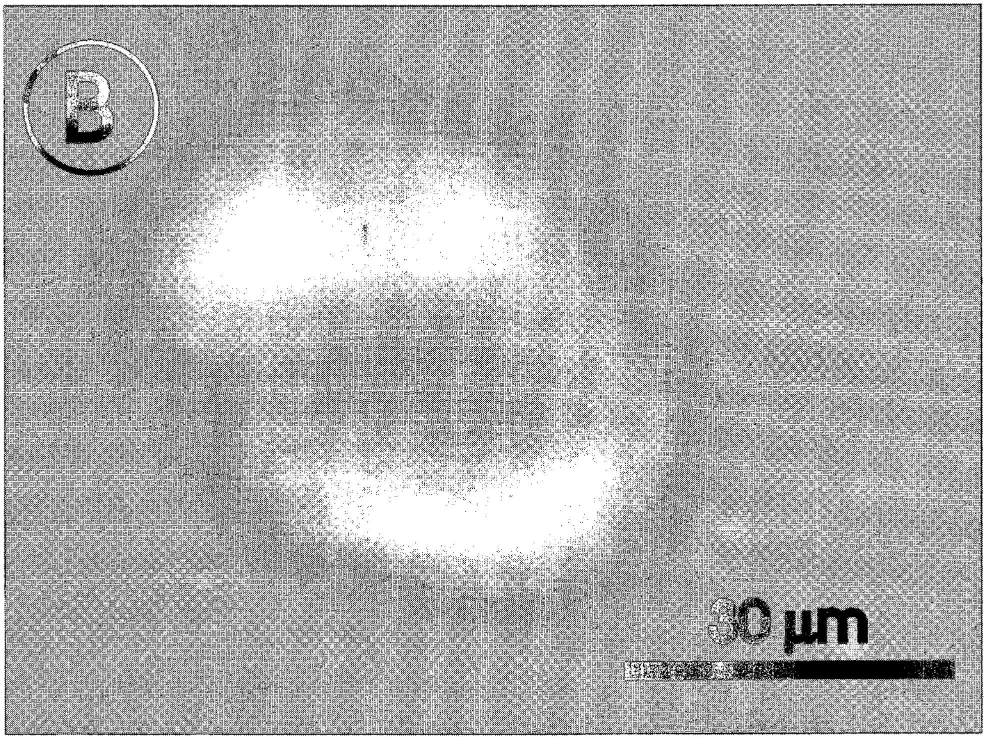
Fig. 3. Zinc $K\alpha$ (A) and bromine $K\alpha$ (B) X-ray maps obtained from the fluid inclusion shown in Figure 1. The approximate outline of the inclusion is indicated by the dashed line in A. Signal intensity is related to the concentration of the element, and to the thickness and structure of the fluid inclusion. The distribution of Zn within the fluid inclusion is essentially identical to that of Br. Note that the position of the vapor bubble, which contains no detectable elements, is resolvable on these maps.


A


B
30 µm

The X-ray maps indicate that Zn and Br have nearly identical distributions, which corresponds to the fluid-dominant regions in the inclusions. We conclude that zinc, like bromine, is concentrated in the aqueous fluid and is not a major component in any of the daughter crystals present. The inclusions were estimated from XRF spectra to contain approximately 0.4 wt% zinc within aqueous solutions by comparison with standard solutions of known concentration.

Synchrotron X-ray-fluorescence analysis of the fluid inclusions indicate that XAFS spectra may also be obtained for Mn, Fe, Pb and Br. Future studies will be aimed at investigating the structural environment surrounding these inclusion components. However, interpretation of the aqueous species of iron in type-1 fluid inclusions will be complicated by the presence of the iron-rich daughter mineral (Fig. 1).

Collection of XAFS data

Room-temperature Zn *K*-edge XAFS spectra were collected in the fluorescence mode from individual fluid inclusions, using a 30 mm^2 Si(Li) energy-dispersion detector at beamline X26A. The detector was mounted at 90° to the incident beam (*i.e.*, incident and takeoff angle at 45°). This geometry of the detector is used in synchrotron fluorescence experiments to minimize the background radiation that arises from Compton scattering. In order to obtain the desired counting statistics for reliable data-fitting, it was necessary to acquire a single spectrum for up to six hours.

The X-ray storage ring at the NSLS operated at 2.54 GeV and between 130 to 230 mA of beam current. A single Si(111) channel-cut monochromator and a 8:1 ellipsoidal Al (Pt-coated) focusing mirror were used. The monochromator has an operating range of 4–20 keV and an energy bandwidth of 10^{-4} ($\Delta E/E$). The focusing mirror was used to increase the flux of photons per area on the sample and also to reject higher harmonics of Zn *K*-edge because the high-energy cutoff of the mirror is about 14 keV. In addition, fine slits were used to collimate scattered portions of the X-ray beam (~50 × 50 μm), giving a flux of about 1 × 10^5 photons per second at a beam current of 230 mA. The high-resolution X–Y–Z–θ stage and an optical microscope were used for sample positioning. The surface of the doubly polished quartz wafer containing the fluid inclusions was positioned at 45° to the beam and detector. An ion chamber filled with helium and located downstream from a slit assembly served for normalization of the intensity of the incident beam.

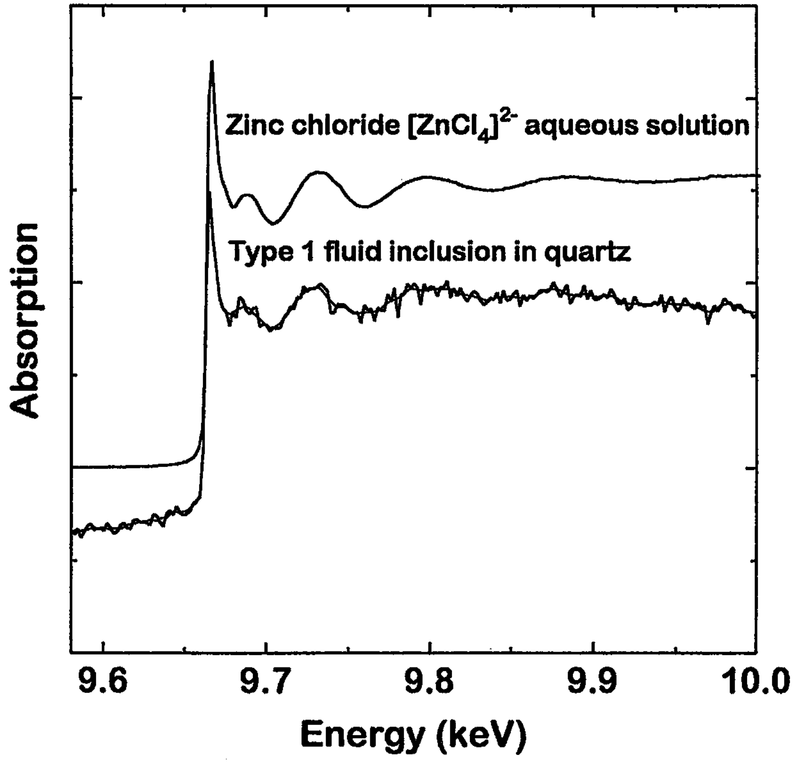


FIG. 4. Zn *K*-edge XAFS spectra collected in fluorescence mode from a zinc chloride ($ZnCl_4^{2-}$) aqueous solution in a SiO_2-glass capillary tube and from a type-1 fluid inclusion. The inclusion spectrum is shown by the jagged solid line, and the smooth solid line represents the smoothed spectrum using two-point averaging method.

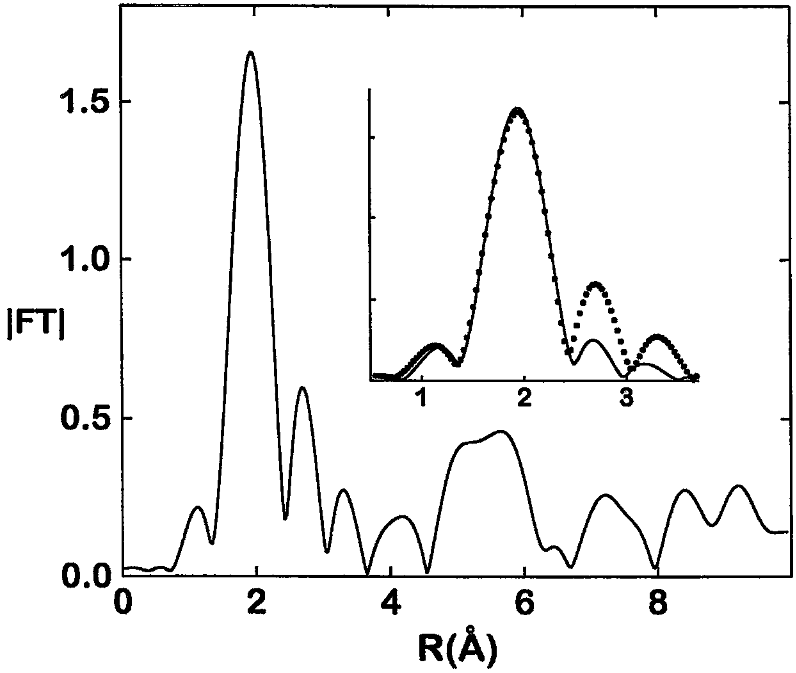


FIG. 5. The magnitude of the Fourier transform (FT) of the $k^2\chi$ data. The inset shows the fit (solid line) of the FT data (points) in the 1.3–2.6 Å range using data based on a $ZnCl_4^{2-}$ model and generated using the program FEFF 5.

XAFS data analysis

The X-ray absorption signal in Figure 4 was normalized with respect to the intensity of the ring current I_{ring} and not I_0, which is customarily the case, because of the greater noise in the latter. Nevertheless, I_{ring} and I_0 were found to be closely correlated. Two-point averaging was used to eliminate some of the noise in the signal.

The absorption data obtained from one inclusion (designated GRMT 2), together with the data obtained from the zinc chloride ($ZnCl_4^{2-}$) aqueous solution, are shown in Figure 4. The data analysis was performed using the *University of Washington package* (see Sayers & Bunker 1988). A simple second-order polynomial fitting was used to remove the pre-edge background, and a cubic least-squares-spline approximant to the data was used, over the range 28–340 eV above the edge, to remove the above-edge background in the smoothed χ data from GRMT 2. The Fourier transforms were calculated from $k^2\chi$ data, using a modified Hanning function-type window over the 3.0–9.3 $Å^{-1}$ range. Additional details concerning the procedures of data analysis can be found in Sayers & Bunker (1988). Nonlinear least-squares fitting based on the Lavenberg-Marquardt method was used, in conjunction with spectra generated using the computer program FEFF 5 (Mustre de Leon *et al.* 1991), on the Fourier-transform data (Fig. 5).

RESULTS AND DISCUSSION

Zinc *K*-edge absorption spectra were obtained from five separate fluid inclusions and from the prepared zinc chloride ($ZnCl_4^{2-}$ and $ZnCl_2^0$) aqueous solutions held within SiO_2-glass capillary tubes. Duplicate spectra were obtained from two fluid inclusions. Data analysis was only performed on the spectra obtained from GRMT 2, which produced the highest signal-to-noise ratio. Except for varying degrees of noise, the absorption spectra obtained from all fluid inclusions were found to be identical. There is also close agreement between the spectra obtained from the zinc chloride solution in the capillary and those of the fluid inclusions (Fig. 4).

The color of the halite daughter crystals and the inclusion brine changed from colorless to yellow-brown during exposure to synchrotron X-rays (Fig. 1). Heating to 400°C caused these inclusions to return to their original colorless state, which indicates that the change is not due to an oxidation reaction. We suggest that the beam-induced change in color in the inclusion is due to the formation of F-color centers.

Inclusion GRMT 2 is situated 5 μm below the polished surface of the quartz host. It is approximately ellipsoidal in shape, with dimensions of 60 × 24 × 20 μm. After subtracting the volume of the vapor bubble and the halite daughter crystal, the volume of the aqueous solution is estimated to be about 1.2 (± 0.1) × 10^{-11} mL.

Analysis of the Fourier-transform data indicates that the dominant aqueous species of zinc in the inclusions studied is $ZnCl_4^{2-}$, having a Zn–Cl bond length of 2.33 ± 0.01 Å, a coordination number of 4.2 ± 0.4 atoms, and a mean-square relative displacement of the atoms of 0.004 ± 0.001 $Å^2$. Our measured Zn–Cl bond length of 2.33 Å is comparable to the 2.30 Å Zn–Cl bond length in $ZnCl_2$ (Oswald & Jaggi 1960). The longer bond-length of Zn–Cl in the aqueous zinc species may be due to less effective splitting of 3p-derived t_{2g} and e_g bonding in Cl *versus* antibonding orbitals of the ligand field (Crerar *et al.* 1985).

Figure 5 shows excellent agreement between the Fourier transform of the XAFS spectra (points) and the theoretical transform data for $ZnCl_4^{2-}$ (solid line) generated using FEFF 5. The diffuse peak located at approximately 5.5 Å in Figure 5 may be due to the interaction of $ZnCl_4^{2-}$ molecules among one another or with other transition metal complexes. We attribute the slightly enhanced intensity of the peak at 2.8 Å in the Fourier data to noise because only the amplitude of this feature is substantially reduced when the Fourier transform window over the $k^2\chi$ data is reduced by about 10%. The close match between spectra obtained from the zinc chloride test solutions in the capillary and those obtained from the inclusion also suggests that the zinc complex in the inclusion is $ZnCl_4^{2-}$.

The presence of a tetrahedral chlorozinc complex ($ZnCl_4^{2-}$) in type-1 inclusions is consistent with the results from experimental (Ruaya & Seward 1986) and laser Raman scattering studies (Morris *et al.* 1963, Easteal *et al.* 1983) of zinc complexation in aqueous solutions having high chloride/zinc stoichiometries. If the stability studies of chlorozinc complexes of Ruaya & Seward (1986) and others can be generalized to complex brines trapped in inclusions, then our results can be used to infer the nature of zinc complexation for the type-1 fluid inclusions at ore-forming temperatures. Thus at temperatures greater than 350°C, the inclusion brine is dominated by charge-neutral zinc complexes ($ZnCl_2^0$).

Although X-ray-fluorescence spectra reveal the presence of bromine (Fig. 2), our theoretically generated Fourier-transform data for various zinc bromide complexes do not match the experimental data. This is consistent with previous studies, which suggest that bromine is not an important ligand in such hydrothermal solutions (Brimhall & Crerar 1987). It is unlikely that another species such as a mixed chlorobisulfide complex (Tossell & Vaughan 1993) or a contact ion-pair is responsible for the observed XAFS data because for all atomic or ionic types, other than the lightest ones ($Z < 5$), that may be arranged in some structural configuration around the central ion of zinc, there should be an associated peak in the Fourier-transform data. Since we see no evidence for any peaks other than those associated with the chlorine ions, we conclude that zinc is coordinated only by chlorine. Furthermore, our determined value for the Debye–Waller factor is consistent with Raman measurements of similar aqueous complexes of zinc (Quicksall & Spiro 1966). In contrast, various dimers and mixed complexes should yield higher values for the Debye–Waller factor, reflecting larger structural disorder.

The present sensitivity of micro-XAFS precludes its application to low concentrations of solutes (<10 ppm), which are typical of metals in many types of hydrothermal ore-forming fluids (Helz *et al.* 1993). Nevertheless, with the current limits of detection, one is capable of resolving the local structure of a wide range of metal complexes in metal-rich fluid inclusions that are characteristic of some granite-related ore deposits (Anderson *et al.* 1989, Heinrich & Ryan 1992). We anticipate that more dilute solutions and smaller fluid inclusions will be measurable in the near future as brighter synchrotron X-ray sources become operational. Also, although atomic displacements due to thermal disorder tend to dampen the XAFS signal (Crozier *et al.* 1988), it may be possible to collect XAFS spectra from *in situ* fluid inclusions at ore-forming temperatures with the aid of a heating stage. Acquisition of XAFS data from fluid inclusions over a range of temperatures is currently in progress.

CONCLUSIONS

We have for the first time measured and analyzed micro-XAFS spectra emitted from a transition-metal complex in individual, unopened fluid inclusions. The oscillations in the X-ray-absorption coefficient contain much quantitative information about the local atomic structure surrounding the absorbing zinc atoms in the fluid. In agreement with previous work on the speciation of zinc in chloride solutions with high Cl:Zn ratios (Barnes 1979, Ruaya & Seward 1986), our results show that, at room temperature, the dominant complex of zinc in the type-1 fluid inclusions is $ZnCl_4^{2-}$, having a Zn–Cl bond length of 2.33 Å.

Analysis of complexes in fluid inclusions by the combination of XAFS and X-ray microbeam techniques provides a direct means of determining the structural properties of metal-bearing species in paleohydrothermal solutions. The formation of metal-carrying aqueous complexes depends upon many variables. The values of many of these variables are not well known in hydrothermal systems and must be approximated in hydrothermal experiments. Our direct approach of structural determination of transition-metal complexes in natural fluid inclusions eliminates some of the uncertainties about fluid chemistry that are inherent in hydrothermal experiments of simple model solutions. Data on the speciation and structure of transition-metal complexes in crustal fluids are relevant to the study of reaction kinetics in fluid-rock interaction (Lasaga 1984, Rickard 1991) and to an understanding of the transport and deposition of ore metals (Brimhall & Crerar 1987). Lower concentrations of metals in fluid inclusions will be measurable by XAFS as brighter and more focused X-ray beams become available.

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REFERENCES

ANDERSON, A.J. & BODNAR, R.J. (1993): An adaptation of the spindle stage for geometric analysis of fluid inclusions. *Am. Mineral.* **78**, 657-664.

________, CLARK, A.H., MA, XIN-PEI, PALMER, G.R., MACARTHUR, J.D. & ROEDDER, E. (1989): Proton-induced X-ray and gamma-ray emission analysis of unopened fluid inclusions. *Econ. Geol.* **84**, 924-939.

________, MAYANOVIC, R.A., BODNAR, R.J., MAVROGENES, J.A., BAJT, S., RIVERS, M.L. & SUTTON, S.R. (1993): The first study of aqueous species in inclusion fluids using X-ray absorption spectroscopy. *Geol. Soc. Am., Program Abstr.* **25**, A-316.

APTED, M.J., WAYCHUNAS, G.A. & BROWN, G.E. (1985): Structure and specification of iron complexes in aqueous solutions determined by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **49**, 2081-2089.

BAES, C.F., JR. & MESMER, R.E. (1976): *The Hydrolysis of Cations.* John Wiley & Sons, New York, N.Y.

BARNES, H.L. (1979): Solubilities of ore minerals. *In* Geochemistry of Hydrothermal Ore Deposits (2nd edition, H.L. Barnes, ed.). Wiley-Interscience, New York, N.Y.

BOIRON, M. & DUBESSY, J. (1994): Determination of fluid inclusion compositions. *In* Fluid Inclusions in Minerals: Methods and Applications (B. De Vivo & M.L. Frezzotti, eds.). Short Course of the working group (IMA) "Inclusions in Minerals" (Pontignano–Siena, 1–4 September, 1994), 45-72.

BOURCIER, W.L. & BARNES, H.L. (1987): Ore solution chemistry. VII. Stabilities of chloride and bisulfide complexes of zinc to 350°C. *Econ. Geol.* **82**, 1839-1863.

BRAITSCH, O. & HERRMANN, A.G. (1963): Zur Geochemie des Broms in salinaren Sedimenten. I. Experimentelle Bestimmung der Br-Verteilung in verschiedenen natürlichen Salzsystemen. *Geochim. Cosmochim. Acta* **27**, 361-391.

BRIMHALL, G.H. & CRERAR, D.A. (1987): Ore fluids: magmatic to supergene. *In* Thermodynamic Modelling of Geological Materials: Minerals, Fluids and Melts (I.S.E. Carmichael & H.P. Eugster, eds.). *Rev. Mineral.* **17**, 235-321.

BUBACK, M. (1981): Spectroscopic investigations of fluids. *In* Chemistry and Geochemistry of Solutions at High Temperatures and Pressures (D.T. Rickard & F.E. Wickman, eds.). *Phys. Chem. Earth* **13-14**, 345-356.

CRERAR, D., WOOD, S., BRANTLEY, S. & BOCARSLY, A. (1985): Chemical controls on solubility of ore-forming minerals in hydrothermal solutions. *Can. Mineral.* **23**, 333-352.

CROZIER, E.D., REHR, J.J. & INGALLS, R. (1988): Amorphous and liquid systems. *In* X-ray Absorption, Principles, Applications, Techniques of EXAFS, SEXAFS and XANES (D.C. Koningsberger & R. Prins, eds.). John Wiley & Sons, New York, N.Y.

DREIER, P. & RABE, P. (1986): EXAFS-study of the Zn^{2+} coordination in aqueous halide solutions. *In* EXAFS and Near Edge Structure IV, Vol. 2 (P. Lagarde, D. Raoux, & J. Petiau, eds.). *J. de Physique* **47**, C8, 809-812.

EASTEAL, A.J., GIAQUINTA, P.V., MARCH, N.H. & TOSI, M.P. (1983): Chemical effects in diffusion and structure of zinc chloride in aqueous solution. *Chem. Phys.* **76**, 125-128.

EISENBERGER, P. & KINCAID, B.M. (1975): Synchrotron radiation studies of X-ray absorption spectra of ions in aqueous solutions. *Chem. Phys. Lett.* **36**, 134-136.

GIAQUINTA, P.V., TOSI, M.P. & MARCH, N.H. (1983): Coordination chemistry and ionic solvation in divalent metal halide aqueous solutions. *Phys. Chem. Liq.* **13**, 1-24.

HAASE, G., GERSTENBERGER, H. & WERNER, C.D. (1987): Rb–Sr geochronology of granites from the Saechsisches Granulitgebirge. *In* ZFI-Mitteilungen (AdW der DDR, ZFI Leipzig). *Contributions to the Geology of the Saxonian Granulite Massif* **133**, 89-97.

HALL, D.L. & STERNER, S.M. (1993): Preferential water loss from synthetic fluid inclusions. *Contrib. Mineral. Petrol.* **114**, 489-500.

HAYAKAWA, S., GOHSHI, Y., IIDA, A., AOKI, S., & SATO, K. (1991): Fluorescence X-ray absorption fine structure measurements using a synchrotron radiation X-ray microprobe. *Rev. Sci. Instrum.* **62**, 2545-2549.

HEINRICH, C.A. & RYAN, C.G. (1992): Mineral paragenesis and regional zonation of granite-related Sn–As–Cu–Pb–Zn deposits: a chemical model for the Mole Granite district (Australia) based on PIXE fluid inclusion analyses. *In* Water-Rock Interaction (Y.K. Kharaka & A.S. Maest, eds.). Balkema, Rotterdam, The Netherlands (1583-1588).

———— & SEWARD, T.M. (1990): A spectrophotometric study of aqueous iron (II) chloride complexing from 25 to 200°C. *Geochim. Cosmochim. Acta* **54**, 2207-2221.

HELZ, G.R., CHARNOCK, J.M., VAUGHAN, D.J. & GARNER, C.D. (1993): Multinuclearity of aqueous copper and zinc bisulfide complexes: an EXAFS investigation. *Geochim. Cosmochim. Acta* **57**, 15-25.

KAATZE, U. & WEHRMANN, B. (1992): Broadband ultrasonic spectroscopy on aqueous solutions of zinc(II) chloride. I. Kinetics of complexation. *Z. Phys. Chem.* **177**, 9-26.

LAGARDE, P., FONTAINE, A., RAOUX, D., SADOC, A. & MIGLIARDO, P. (1980): EXAFS studies of strong electrolytic solutions. *J. Chem. Phys.* **72**, 3061-3069.

LASAGA, A.C. (1984): Chemical kinetics of water–rock interactions. *J. Geophys. Res.* **89**, 4009-4025.

LI, ZHI-FEN & POPOV, A.I. (1982): Zinc-67 NMR study of zinc ions in water and in some nonaqueous and mixed solvents. *J. Solution Chem.* **11**, 17-26.

MAGINI, M., LICHERI, G., PASCHINA, G., PICCALUGA, G. & PINNA, G. (1988): *X-Ray Diffraction of Ions in Aqueous Solutions: Hydration and Complex Formation.* CRC Press, Boca Raton, Florida.

MAYANOVIC, R.A., ANDERSON, A.J. & BAJT, S. (1995): Development of micro-XAFS: applications to studies of single fluid inclusions. *Physica B* (in press).

MORRIS, D.F.C., SHORT, E.L. & WATERS, D.N. (1963): Zinc chloride and zinc bromide complexes. III. Structures of species in solution. *J. Inorg. Nucl. Chem.* **25**, 975-983.

MUSTRE DE LEON, J., REHR, J.J., ZABINSKY, S.I. & ALBERS, R.C. (1991): *Ab initio* curved-wave X-ray-absorption fine structure. *Phys. Rev.* **B 44**, 4146-4156.

NEILSON, G.W., NEWSOME, J.R. & SANDSTROM, M. (1981): Neutron diffraction study of aqueous transition metal salt solutions by isomorphic substitution. *J. Chem. Soc., Faraday Trans.* **II**, **77**, 1245-1256.

OSWALD, H.R. & JAGGI, H. (1960): Zur Strukur der Wasserfreien Zinkhalogenide. I. Die wasserfreien Zinkchloride. *Helv. Chim. Acta* **43**, 72-77.

PARKHURST, D.A., BROWN, G.E., PARKS, G.A. & WAYCHUNAS, G.A. (1984): Structural study of zinc complexes in aqueous chloride solutions by fluorescence EXAFS spectroscopy. *Geol. Soc. Am., Abstr. Programs* **16**, 618.

QIN, ZHENWEI, LU, FANGQIONG & ANDERSON, A.T. (1992): Diffusive reequilibration of melt and fluid inclusions. *Am. Mineral.* **77**, 565-576.

QUICKSALL, C.O. & SPIRO, T.G. (1966): Raman spectra of tetrahalozincates and the structure of aqueous $ZnCl_4^{2-}$. *Inorg. Chem.* **5**, 2232-2233.

RANKIN, A.H., RAMSEY, M.H., COLES, B., VAN LANGEVELDE, F. & THOMAS, C.R. (1992): The composition of hypersaline, iron-rich granitic fluid based on laser-ICP and synchrotron microprobe analysis of individual fluid inclusions in topaz, Mole granite, eastern Australia. *Geochim. Cosmochim. Acta* **56**, 67-79.

RICKARD, D. (1991): Reaction kinetics in ore formation. *In* Source, Transport and Deposition of Metals (M. Pagel & J.L. Leroy, eds.). Balkema, Rotterdam, The Netherlands (3-6).

ROEDDER, E. (1984): Fluid inclusions. *Rev. Mineral.* **12**.

———— (1991): Fluid inclusion analysis – prologue and epilogue. *Geochim. Cosmochim. Acta* **54**, 495-507.

RUAYA, J.R. & SEWARD, T.M. (1986): The stability of chlorozinc(II) complexes in hydrothermal solutions up to 350°C. *Geochim. Cosmochim. Acta* **50**, 651-661.

SAYERS, D.E. & BUNKER, B.A. (1988): Data analysis. *In* X-ray Absorption, Principles, Applications, Techniques of EXAFS, SEXAFS and XANES (D.C. Koningsberger & R. Prins, eds.). John Wiley & Sons, New York, N.Y.

SEWARD, T.M. (1981): Metal complex formation in aqueous solutions at elevated temperatures and pressures. *In* Chemistry and Geochemistry of Solutions at High Temperatures and Pressures (F. Wickman & D. Rickard, eds.). *Phys. Chem. Earth* **13-14**, 113-129.

SUSAK, N.J. & CRERAR, D.A. (1985): Spectra and coordination changes of transition metals in hydrothermal solutions: implications for ore genesis. *Geochim. Cosmochim. Acta* **49**, 555-564.

TOSSELL, J.A. & VAUGHAN, D.J. (1993): Bisulfide complexes of zinc and cadmium in aqueous solution: calculation of structure, stability, vibrational, and NMR spectra, and of speciation on sulfide mineral surfaces. *Geochim. Cosmochim. Acta* **57**, 1935-1945.

VALYASKHO, M.G. (1956): Geochemistry of bromine in the processes of salt deposition and the use of the bromine content as a genetic and prospecting criterion. *Geochem.* **6**, 570-589.

YAMAGUCHI, T., HAYASHI, S. & OHTAKI, H. (1989): X-ray diffraction and Raman studies of zinc(II) chloride hydrate melts, $ZnCl_2 \cdot RH_2O$ (R = 1.8, 2.5, 3.0, 4.0, and 6.2). *J. Phys. Chem.* **93**, 2620-2625.

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