NATURAL AND SYNTHETIC QUARTZ GROWTH AND DISSOLUTION REVEALED BY SCANNING ELECTRON MICROSCOPE CATHODOLUMINESCENCE

Brian Rusk[1*], Mark Reed[2], David Krinsley[2], Greg Bignall[3], and Noriyoshi Tsuchiya[1]

1Graduate School of Environmental Studies, Tohoku University, Japan
*E-mail: brusk@geo.kankyo.tohoku.ac.jp
2Department of Geological Sciences, University of Oregon, USA
3 Institute for Geological and Nuclear Sciences, Wairakei Research Centre, New Zealand

Scanning electron microscope-cathodoluminescence (SEM-CL) reveals textures in quartz that are not observable using any other technique. CL textures in hydrothermal quartz reflect primary precipitation processes that are modified by subsequent dissolution, deformation, fracturing, or recrystallization. Superposition of multiple textures in individual quartz veins yields complex textures with obscure origins. To infer the processes that form complex CL textures in natural hydrothermal quartz, we analyzed samples from eighteen ore deposits of five types as well as synthetic quartz formed in three flow reactor autoclave experiments conducted at up to 500°C at 30 MPa.

The most common CL texture in hydrothermal quartz is oscillatory euhedral growth zoning, which occurs in all of the deposit types analyzed and in the synthetic hydrothermal quartz. Euhedral growth zones were rare, however, in orogenic gold deposits, probably owing to annealing of primary CL textures caused by quartz recrystallization.

In porphyry copper deposits and epithermal deposits, SEM-CL imaging reveals hydrothermal quartz cut by thin fractures filled with CL-dark quartz. Such textures indicate that these deposits are characterized by multiple stages of fracturing, fluid flow and quartz precipitation. In experimentally grown quartz, and orogenic gold deposits, CL-dark fractures are rare.

CL evidence for quartz dissolution is present in epithermal ore deposits and porphyry copper deposits. Porphyry copper deposits were the only deposit type where rounded and embayed cores of quartz were observed to be overgrown by rims of euhedral quartz. Such dissolution is interpreted to result from cooling of hydrothermal fluids through the zone of retrograde quartz solubility, where fluid cooling leads to quartz dissolution rather than precipitation. No other deposit type analyzed exhibited this texture, suggesting the pressure-temperature conditions necessary for retrograde quartz dissolution may be unique to porphyry copper deposits.

1.Introduction

Scanning electron microscope cathodoluminescence (SEM-CL) reveals textures in quartz that are not seen using any other observation technique (Figure 1). Variations in CL intensity are caused by mineral non-stoichiometry, poor crystallographic ordering, lattice defects, or by the incorporation of trace elements into the quartz crystal lattice [1]. Interpretations of CL textures in quartz veins yield unique insights into the physical and chemical evolution of ancient hydrothermal ore deposits and active geothermal systems [2-5].

We have observed SEM-CL textures in eighteen hydrothermal ore deposits to evaluate the key features of fluid flow in the crust and to compare the physical processes of hydrothermal vein formation across a wide range of P-T conditions. Deposits examined include six porphyry copper deposits (Gaby Sur, Chile; El Abra, Chile; Yerington, NV, USA; Bingham, UT, USA; Bata Hijau, Papau New Guinea; and Butte, Montana, USA), five epithermal deposits (Mclaughlin, CA, USA; Porgera, Papua New Guinea; Butte, Montana, USA; Shuteen, Mongolia; and Bohemia, Oregon, USA), five orogenic gold deposits (Norseman, Australia; Carson Hill, CA, USA; Mt. Charlotte, Kalgoorlie District, Australia; San Bento mine, Minas Gerais, Brazil; and Passagem De Mariana Mine, Oro Preto, Brazil), the massive sulfide deposit in the West Shasta District,

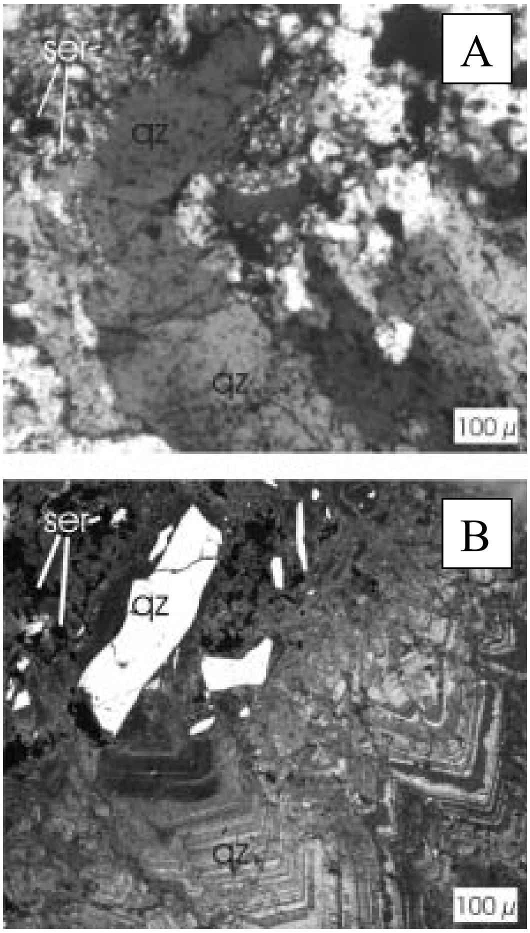

Figure 1. A) Transmitted light image of a pyrite-quartz vein. Image shows that both quartz and sericite are present in the vein, but little more. B) SEM-CL image of the same area shown in A. This image shows a variety of CL textures including evidence for multiple generations of quartz growth.

CA, USA; and a sample of Mississippi Valley-type quartz from the USA.

We also analyzed three synthetic hydrothermal quartz veins experimentally grown in granite from hydrothermal fluids at temperatures and pressures applicable to many hydrothermal and geothermal systems (200 to 500°C and 300 bars). P-T conditions were pre-set in each experiment, in order to produce temperature gradients conducive to quartz precipitation.

Analyzed natural and experimental quartz display a wide variety of CL textures. While it is difficult to interpret the processes responsible for all CL textures observed, this study offers a comparison of CL textures observed in different deposit types and also compares natural hydrothermal quartz with quartz grown under controlled conditions in the laboratory. From these comparisons, we gain insight into processes that are unique to specific hydrothermal deposits, and into other processes that are ubiquitous among hydrothermal deposits. We also gain insight into the origin of many CL textures based on known conditions of formation of the examined ore deposits.

2. Methods

SEM-CL images were collected at the University of Oregon using a JSM 6300V SEM with an Oxford Instruments mirror-type CL detector and a Hamamatsu R374 photomultiplier tube. Carbon coated sections were analyzed at 10 KV with a beam current between 0.1 and 120 nA, depending on the luminosity of the quartz. We use the terms CL-dark, CL-gray, and CL-bright to refer to quartz of varying intensity in a single image. These terms are useful only relative to one another in a single image, as adjustments of SEM operating conditions will cause increases or decreases in apparent intensities of quartz luminescence.

Hydrothermal quartz was experimentally synthesized at the Graduate School of Environmental Studies, Tohoku University, in an AKICO, high-temperature/pressure flow autoclave system. The autoclave consists of three, one-meter-long Hastelloy-C reactor tubes [6] in which temperature can be independently controlled. Inside the autoclave, an artificial fracture is created by spacing pre-cut blocks of granite (Iidate Granite, Japan) about 5 mm apart along the entire length of the autoclave. Distilled water is heated and injected into the pressurized system, where the fluid flows down a pre-set temperature gradient. The heated distilled water initially dissolves quartz from the host granite, and then upon fluid cooling, quartz precipitates in the artificial fracture forming a vein.

Three hydrothermal experiments were carried out at a constant pressure of 300 bars, with a constant fluid flux of 1 cm^3/min, and a constant temperature gradient that varied among the experiments. Flow-through experiments lasted from two days to two weeks. In one experiment, quartz apparently precipitated upon fluid heating in the zone of retrograde quartz solubility (between about 400 and 425°C), while in the other two experiments quartz precipitated as fluids cooled from temperatures as high as 500°C to temperatures below 200°C.

Table 1. Textures observed in eighteen ore deposits and 3 experimental veins. Numbers in parentheses are number of deposits analyzed.

-- Not observed R- Rare	Crystallization			Recrystal-lization	Fracturing			Dissolution	
P- Present C- Common A-Abundant	Chacedonic growth zones	Bi-pyramidal growth zones	Euhedral growth zones	Homogenous or mottled texture	CL-dark fractures	CL-bright fractures	Breccia-tion	Rounded cores with overgrowths	Splatter and cobweb
Porphyry copper deposits (6)	-	-	C	P	A	R	-	P	C
Epithermal deposits (5)	P	-	A	-	C	-	P	-	P
Orogenic gold deposits (5)	-	-	R	A	R	-	R	-	-
Mississippi Valley type deposits (1)	-	-	A	-	R	-	-	-	-
Massive sulfide deposits (1)	-	P	C	C	-	-	C	-	-
Experimental quartz (3)	-	-	A	-	-	-	-	-	-

3. Results

3.1 CL textures Veins in all natural hydrothermal ore deposits analyzed contain primary CL textures modified by at least one secondary texture. Most deposits show evidence for multiple secondary processes. Primary CL textures develop within a growing quartz grain as a result of fluid temperature, pressure, composition, and rate of crystallization. Primary precipitation textures observed include: 1) euhedral growth zones (Figures 2A, B, C, D, F), 2) chalcedonic textures (Figures 2C), and 3) doubly terminated quartz crystals (Figure 2B, Table 1). Many primary textures are modified by secondary textures that form as a result of dissolution, dilation, fracturing, recrystallization, and further quartz precipitation. Secondary textures identified in veins include: 1) splatter and cobweb texture (fracturing, dissolution, and precipitation) (Figure 2F), 2) CL-dark or CL-bright fractures (fracturing, dilation, and precipitation) (Figure 2G), 3) quartz overgrowth on remnant quartz cores (dissolution and precipitation) (Figure 3), 4) mottled and homogenous texture (recrystallization) (Figure 2E), and 5) microbrecciation (Table 1)

3.2 Crystallization textures We identified euhedral growth zones in all deposit types and in experimentally grown quartz (Figure 2A, B, C, D, F). Growth zones are manifested as alternating bands of CL-bright and CL-dark quartz commonly parallel to the external terminations of the crystal. In many quartz grains however, euhedral growth zones are apparent using CL, but the host crystal does not optically display euhedral terminations. Variations among growth band styles exist within and among the examined samples. Width of the growth bands vary considerably, as do the shape, the intensity of luminescence of the growth bands, and the contrast in intensity among the growth bands. These variations reflect differences in the conditions of quartz precipitation, however no studies have related growth zones in quartz to specific geologic events.

3.3 Fracturing textures CL-dark fractures are common in porphyry copper deposits and in epithermal ore deposits, but they are rare in the other deposit types and in experimentally produced quartz (Figure 2). CL-dark and CL-bright bands vary in size from sub-micron to millimeters in width and are the result of fracturing of previously precipitated quartz. These bands are commonly coincident with trails of fluid inclusions and may be filled with inward-oriented euhedral quartz crystals indicating fracturing of quartz, followed by dilation, fluid infiltration, and quartz precipitation. Fractures healed by quartz that is brighter than the fractured host quartz (i.e CL-bright bands) were observed only in early veins from the porphyry copper deposit in Butte, Montana. A study of CL intensity in Butte hydrothermal quartz suggests that CL-bright quartz precipitated from fluids hotter than the fluids that precipitated CL-dark quartz [7].

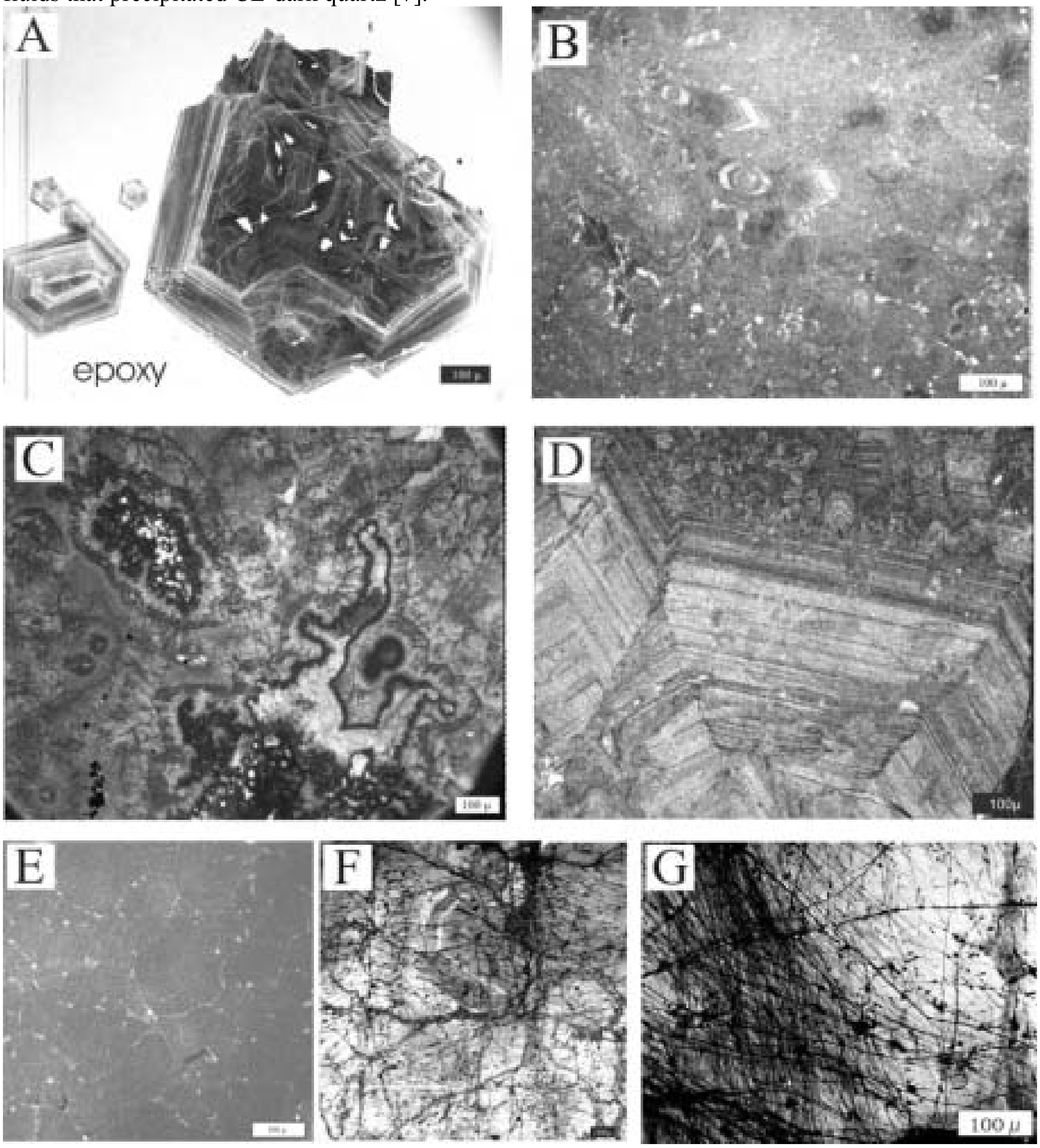

Figure 2. All images are SEM-CL images and show only vein quartz, except where noted. All scale bars are 100 microns. A) Euhedral growth zones in experimentally grown quartz. Bright spots within the large crystal are holes. B) Bi-pyramidal euhedral quartz from the massive sulfide deposit from West Shasta, CA. C) Complex chalcedonic and spheroidal textures in quartz from the McLaughlin epithermal deposit CA. D) Euhedral growth zones in vein quartz from an epithermal Main Stage vein in Butte, MT. E) Homogenous CL-dark quartz from the San Bento orogenic gold deposit in Minas Gerais, Brazil F) Splatter and cobweb

texture overprinting vein quartz with euhedral growth zones from the Shuteen epithermal deposit, Mongolia, G) Intense CL-dark fracturing of CL-bright quartz in a vein from the porphyry copper deposit in Butte, MT.

3.4 Recrystallization textures Evidence for recrystallization of quartz is abundant in all orogenic gold deposits, and also present in porphyry copper deposits and the single massive sulfide deposit analyzed (Figure 2E). Quartz recrystallization is inferred from homogenous or mottled CL texture, "ghosty appearance" of CL textures, or very low contrast between growth zones. It is, in some cases, difficult to infer whether the quartz initially precipitated with little or no CL texture or whether a previously existing CL-texture was subdued by annealing. This issue is addressed below.

3.5 Dissolution textures Dissolution textures were recognized only in vein samples from porphyry copper deposits and epithermal deposits. Evidence for dissolution includes rounded embayed CL-bright quartz cores with CL-dark overgrowths (Figure 3), resulting from dissolution of pre-existing quartz, followed by precipitation of later quartz into the space created by dissolution. We identified this texture only in the porphyry copper deposit in Butte, Montana. The texture has also been identified in veins from Bingham Canyon, Utah [8].

Quartz dissolution is also suggested by "splatter and cobweb" texture, wherein patches of CL-dark quartz in the shape of paint splatters are connected by variably oriented, anastomosing, and bifurcating bands of CL-dark quartz. These cobweb-like networks of CL-dark quartz vary from dense networks with up to 30% CL-dark quartz in a given area, to sparse CL-dark splatters, with few connecting CL-dark cobwebs, and <5% CL-dark quartz (Figure 2F). Splatter and cobweb texture is the result of quartz dissolution focused along microfractures, followed by precipitation of CL-dark quartz into the newly created cavities. We have identified "splatter-and-cobweb" texture in multiple porphyry copper deposits and epithermal deposits.

4. Implications

4.1 Natural hydrothermal deposits This study yields important insight into the origins and interpretations of CL textures as well as into the processes active in forming hydrothermal systems. Euhedral growth zones are found in quartz from all deposit types which is inferred to have precipitated over a wide range of temperatures from 150 to 650°C. This indicates that under a wide range of geologic conditions, quartz precipitating from hydrothermal fluids will form euhedral growth zones.

While euhedral growth zones occur in quartz from most deposit types, they are conspicuously rare in orogenic greenstone-gold deposits where homogenous and mottled textures dominate. Homogenous and mottled CL textures are characteristic of quartz from metamorphic rocks [9, 10], where the lack of texture is likely to be the result of annealing of original textures during prolonged exposure to high pressure and temperature. We conclude that annealing is responsible for the lack of CL textures in quartz from orogenic gold deposits, which are subjected to low grade metamorphic conditions.

Homogenous and mottled textures were also identified in the only massive sulfide deposit analyzed and in several porphyry copper deposits. As in metamorphic rocks, these annealed textures are likely the result of redistribution of lattice defects and trace element concentrations in the quartz, due to continued exposure to high pressure and temperature.

Conditions necessary to cause annealing of CL textures are currently unknown, but batch autoclave experiments (Rusk and Sekine, unpublished) show that partial annealing of CL textures occurred in only 10 days in natural epithermal quartz introduced into hydrothermal fluids at 500°C and 500 bars. However, the presence of primary CL textures in quartz veins, that are overprinted by later fracturing and hydrothermal fluid influx indicates that annealing does not always occur in hydrothermal ore deposits. It is possible that annealing results from prolonged exposure to high temperatures and pressures and that the presence of differential stress is important in the annealing of CL textures in quartz.

Evidence for dissolution of quartz, followed by growth of quartz into the newly created space was only identified in porphyry copper and epithermal-style deposits. Dissolution of quartz can result from heating of hydrothermal fluids (Figure 3, path D-C), cooling of hydrothermal fluids through the zone of retrograde solubility (Figure 3, path B-C), or from an increase in pressure (Figure 3, path B-A). While each case must be analyzed individually, Rusk and Reed [2] infer that dissolution in the porphyry copper deposit in Butte MT, (the only deposit where CL-bright cores with overgrowths were observed), is the result of cooling through the region of retrograde quartz solubility, followed by continued cooling of the hydrothermal fluid into the region of prograde quartz solubility (Figure 3, path A-B-C-D). Splatter and cobweb texture, on the other hand, was identified in all porphyry copper deposits and many epithermal deposits. Splatter and cobweb texture may occur as a result of repressurization of the hydrothermal system due to fracture plugging by quartz precipitation. The amount of dissolution is likely to be small because it is limited by the small supply of through-going fluid whose passage is restricted in the now-plugged vein.

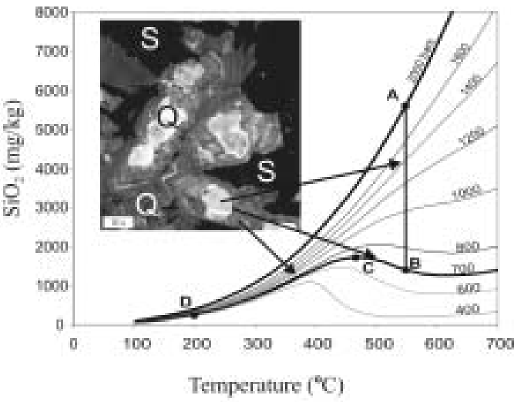

Figure 3. Solubility of quartz in water as a function of temperature at pressures indicated (data from Shock et al., [11]). Path A-B represents an isothermal pressure drop from lithostatic (2000 bars) to near hydrostatic pressure (700 bars) at 550°C causing quartz precipitation. Cooling along path B-C at 700 bars (in the zone of retrograde quartz solubility) leads to dissolution of quartz. Cooling below point C at 700 bars causes quartz to precipitate. Such a depressurization/cooling path is likely to form the rounded and embayed CL-bright cores with CL-dark euhedral overgrowths as observed in the porphyry copper deposit in Butte Montana (inset). In the inset, S is sericite (non-luminescent mineral) and Q is quartz (both CL-bright and CL-dark).

4.2 Experimental quartz Experimental quartz was grown from fluids flowing at a constant flow rate, at a constant pressure, under a constant temperature gradient in a granite fracture. The injection fluid in these experiments was pure distilled water. As no salts were present in the fluid or in the host granite, the fluid contained very little dissolved ions. Although quartz precipitated under slightly different conditions in each experiment, no difference in quartz morphology or CL textures are recognized among the three synthetic veins.

Significantly, euhedral growth zones were ubiquitous in quartz from all three experiments. This indicates that complex behavior such as boiling, change in fluid composition, or fluid temperature are not necessary to produce growth zones of variable CL intensity in quartz. SEM-CL-detectable euhedral growth zones can grow from a dilute fluid under relatively stable conditions. Thus the observation of growth zones of varying intensity in natural quartz does not necessarily indicate significant changes in fluid conditions.

Euhedral growth zones are the most common texture observed in experimentally precipitated quartz, which shows no evidence for quartz recrystallization, fracturing, or dissolution. In contrast, all natural hydrothermal deposits, displayed complex CL-textures wherein vein quartz was recrystallized, fractured, dissolved, or some combination of these. This comparison between natural quartz and experimentally produced quartz indicates that all hydrothermal deposits analyzed have a more complex history than fluid cooling in an open fracture under stable fluid-flow conditions.

Acknowledgements

The authors thank John Dilles, Elizabeth Ronacher, Steve Garwin, and Batkhishig Bayaraa for samples and thoughtful discussion. We also thank Nobuo Hirano and Kotaro Sekine for assistance with the autoclaves. This research was supported by National Science Foundation grants (USA) EAR-9704280, EAR-0001272, EAR-26-6234-02, and by the support of the 21st Century COE program, Tohoku University, Japan.

References

[1]Gotze, J., Plotze, M., Habermann, D., Min. and Pet., **71**, 225 (2001).
[2] Rusk, B.G. and Reed, M.H., Geology, **30** 727 (2002).
[3] Wilkinson, J.J., Boyce, A.J., Earls, G., Fallick, A.E., 1999, Econ. Geol., **94,** 289 (1999).
[4] Penniston-Dorland, S.C., Am. Min., **86,** 652 (2001).
[5] Bignall, G., Sekine, K., and Tsuchiya, N., Geothermics, in press, (2004).
[6] Bignall, G., Hirano, N., Batkhishig, B, Tsuchiya, N., Rusk, B., and Sekine, K, in Proceedings of 11^{th} annual WRI, 615 (2004).
[7] Rusk , B.G., Unpublished Ph.D. dissertation, Univ. of Oregon, 250 p. (2003).
[8] Redmond, P., Einaudi, M.T., Inan, E.E., Landtwing, M.R., and Heinrich, C.A., Geology, **32**, 217 (2004)
[9] Boggs, S., Kwon, Y., Goles, G.G., Rusk, B.G., Krinsley, D., and Seyedolali, A., Jour. of Sed. Res. **72,** 408 (2001).
[10] Seyedolali, A., Krinsley, D., Boggs, S. Jr., O=Hara, P., Dypvik, H., and Goles, G., Geology, **25**, 787 (1997).
[11]Shock, E.L., Helgeson, H.C., and Sverjensky, D.A., Geochim et Cosmochim Acta, **53**, 2157 (1989).