

The influence of water on the environment of transition metals in silicate glasses

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ABSTRACT

The effect of water (= $\text{H}_2\text{O} + \text{OH}$) on the environment of Co^{2+} and Ni^{2+} in albite glass was investigated by electronic absorption spectroscopy. The visible spectra of Co^{2+} -doped glasses change only slightly over the range of water concentrations studied. Co^{2+} is in a distorted tetrahedral environment, producing a dark blue color in the glasses. Up to about 5 wt% water, Ni^{2+} -doped glasses are brown and only minor variations in the spectra are seen. At 5.6 wt% water, however, the color of these glasses changes abruptly from brown to light green and a new type of absorption spectrum is observed. Three bands are observed in the visible spectra of the brown glasses. Two bands near $20\,500\text{ cm}^{-1}$ can be assigned to Ni^{2+} in a distorted octahedral environment. A third band at $15\,500\text{ cm}^{-1}$ could either be due to the distorted octahedral site or to a small amount of tetrahedrally coordinated Ni^{2+} . The spectra of the green glasses with 5.6 and 5.7 wt% H_2O resemble closely spectra of aqueous NiCl_2 -solution containing the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex. The formation of such a hydration shell around transition metals in hydrous silicate melts should strongly effect partitioning of these elements between silicate melts, minerals, and a metal phase. Consideration of ligand field stabilization energies, suggests that hydrated Ni^{2+} is stabilized in the melt such that mineral-melt and metal-silicate melt partition coefficients decrease by one to two orders of magnitude relative to a dry melt at $1100\text{ }^\circ\text{C}$.

INTRODUCTION

Transition metals are the most important compatible trace elements in magmatic systems. The mineral-melt partitioning of the first series transition elements is crucial for understanding major Earth-forming processes such as the evolution of the mantle and the crust. Modeling of core formation requires the understanding of the distribution of Co and Ni between silicate melt and metallic liquid. The partitioning of transition metal ions between silicate melt and minerals or metal cannot be appropriately modeled by elastic strain energy models because of ligand field effects and strong covalent bonding interactions (e.g., Figgis 1966; Burns 1993).

Although numerous recent studies exist on the environment of transition metals in magmatic melts and glasses (e.g., Burns 1993), little information is available on the effect of H_2O on the coordination sphere and on the partitioning of these elements. Water (= $\text{H}_2\text{O} + \text{OH}^-$) is the most important volatile component of natural magmatic systems and influences physical and chemical properties of aluminosilicate melts to a great extent (e.g., Burnham 1979). High P and high T measurements of water speciation in aluminosilicate melts show that both hydroxyl groups and H_2O molecules are stable, and hydroxyl groups dominate even at water contents up to 10 wt% (Nowak 1995; Nowak and Behrens 1995; Shen and Keppler 1995). This result implies that dissolved water depolymerizes the structure of aluminosilicate melts very effectively and that molecular H_2O is a possible ligand at

high water contents. Watson (1976), Hart and Davis (1978), and Mysen and Virgo (1980), suggested that mineral-silicate melt partition coefficients of transition metals depend on the melt composition and thus on the degree of melt polymerization.

Infrared (IR), Raman, and nuclear magnetic resonance (NMR) spectroscopy mostly probe network-forming cations. Little is known on the effect of water on network modifiers such as alkalis and alkaline earths in glasses. NMR and X-ray absorption spectroscopy (XAS) work by Kohn et al. (1989; 1990) suggest major changes in the environment of network modifiers if water is added to the glass. Transition metals may serve as a model for other network modifiers and can easily be studied by electronic absorption spectroscopy, i.e., by investigating electronic transitions in the near IR, visible, and UV absorption spectra.

We studied the structural environments of Ni^{2+} and Co^{2+} in albitic glasses quenched from dry and hydrous melts using electronic absorption spectroscopy. This is the only suitable method to investigate the incorporation of transition metal ions in quenched silicate melts aside from XAS and Mössbauer spectroscopy. Furthermore it is experimentally simple, insensitive to disorder, and theoretically well understood. The electronic absorption spectra of Co^{2+} and Ni^{2+} in silicate glasses are intense and show enough bands to derive the complete set of crystal-field parameters (Keppler 1992). Furthermore, spectra of Co^{2+} and Ni^{2+} in high polymerized albite glass-

es resemble those in depolymerized albite-diopside glass (Keppler 1992). Therefore, albite glass may serve as a simple model system for a wide range of silicic to basic compositions.

EXPERIMENTAL METHODS

Preparation of CoO- and NiO-doped albite glasses

Starting materials were high-purity oxides and carbonates (SiO₂, Al₂O₃, Na₂CO₃, NiO, or Co₃O₄). These compounds were mixed and ground in an agate mortar under acetone. Batches of 5 g of the starting mixture were slowly decarbonated by heating in a platinum crucible with lid to 1000 °C at a rate of 50 °C/h. After decarbonatization, the oxide mixtures were melted in a MoSi₂ furnace at 1300 °C for 3 to 4 h and then at 1600 °C for 4 h. The samples were rapidly quenched by dropping the crucible into cold water with an estimated quench rate of 200 °C/s. Homogeneous, nearly bubble-free glasses were produced.

Hydration of CoO- and NiO-doped albite glasses

The dry glasses doped with 1 wt% CoO or 0.5 wt% NiO were crushed in a steel mortar and sieved to obtain grain sizes of <500 μm. These powders were stored at 150 °C in a drying furnace to avoid adsorption of H₂O. Then platinum capsules (diameter = 3.5 mm; length = 30 mm; wall thickness = 150 μm) were filled with 250 mg of powder and known amounts of doubly distilled water. For synthesizing NiO-doped hydrous glasses, 4 to 6 mg AgO-powder wrapped in platinum foil were added to the charge to maintain oxidizing conditions and to minimize alloying of Ni with the platinum capsule during the experiment. The capsules were then cooled with water and welded shut. The sealed capsules were checked for possible leaks by heating at 150 °C for 1 h.

The hydration experiments were performed in TZM (TZM = Ti-Zr-Mo-alloy) autoclaves pressurized with Ar. Experiment conditions were 350 to 2200 bars, 1015 to 1165 °C, and 24 to 168 h. The furnace temperature near the vessel was measured by a Pt-PtRh thermocouple with an accuracy of ±10 °C. The temperature of the sample was calibrated using a certified Ni-CrNi thermocouple (Heraeus Sensor) in the interior of the vessel. The accuracy of the sample temperature is better than ±10 °C. The pressure was monitored with a strain-gauge manometer with an accuracy of ±50 bar. At the *P* and *T* conditions of the experiments the melts were water-saturated or -undersaturated (Behrens 1995), and the experiment durations were sufficient to allow complete homogenization of the water in the melt (Nowak and Behrens 1997). Samples were quenched isobarically with about 200 °C/s by dropping the capsules into the water-cooled part of the vessel.

Chemical analysis

The bulk chemistry of the quenched dry glasses and the CoO and NiO concentrations of the hydrated glasses were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Jobin Yvon

ISA JY24. The homogeneity of the transition metal concentrations in the hydrated glasses was checked by using electron microprobe (Cameca SX50). The samples were analyzed under 15 kV acceleration voltage, 15 nA sample current, and 20 s counting time, with albite and Co- and Ni-metal standards and PAP correction procedures. We used a defocused beam (30 μm) to minimize alkali loss. Transition metal concentration-distance profiles consisting of 20 individual analyses were taken perpendicular to the platinum capsule walls across the slices.

Spectroscopic measurements

Doubly polished plates (250 and 500 μm thick) were prepared from the dry and hydrous CoO- and NiO-doped glass samples. A Bruker IFS 120 Fourier-transform spectrometer equipped with an A 590 microscope was used to collect 200 scans for each spectrum.

Water content of the glass samples were determined from near-infrared (NIR) spectra. Measurements in the range from 2000 to 10000 cm⁻¹ were carried out using the microscope, a tungsten lamp, a CaF₂ beam splitter, and a narrow band MCT detector. The homogeneity of the water content was tested by three individual measurements at the rim and in the middle of each sample. In the case of samples that contained bubbles, we took care to measure bubble-free regions.

For the samples with low water content, the peak height of the fundamental O-H stretching vibration at about 3500 cm⁻¹ and the linear molar extinction coefficient for albite glass (66 L/mol cm⁻¹) determined by Silver and Stolper (1989) were used to calculate the water contents. The linear absorbances of the H₂O- and the OH-combination modes at 5230 and 4500 cm⁻¹, respectively, were used to determine the H₂O and OH concentrations of the samples containing higher water contents. Densities and extinction coefficients for hydrous albite glasses were taken from Behrens et al. [1996; ε_{OH} = 1.28 L/mol·cm⁻¹; ε_{H₂O} = 1.49 L/mol·cm⁻¹; ρ (g/L) = 2384 - 13.8 c_{water} (wt%)]. Total water contents were obtained by summation.

For the hydrated NiO-doped glasses a linear tangent was fitted to the minima at both sides of the absorption band at 5230 cm⁻¹ to define the baseline. Extrapolation of this tangent toward lower wavenumbers was used to determine the maximum height of the band at 4500 cm⁻¹. The background of the water absorption bands of the CoO-doped glasses is influenced by the NIR electronic absorption bands of Co²⁺ (Fig. 1). Thus we used a Gaussian fit with maximum at about 5350 cm⁻¹ to get an estimate of the background. This procedure increases the error in the peak heights of the two bands, especially at 4500 cm⁻¹. We estimate that the OH concentration is underestimated by 10% relative to the true value.

A tungsten lamp, a Qz-beam splitter with dielectric coating, and an Si diode were used to monitor electronic absorption spectra from 8000 to 20 000 cm⁻¹. For the high frequency region (10 000 to 34 000 cm⁻¹), an Xe-filled electric arc lamp and an Al-coated quartz beam splitter

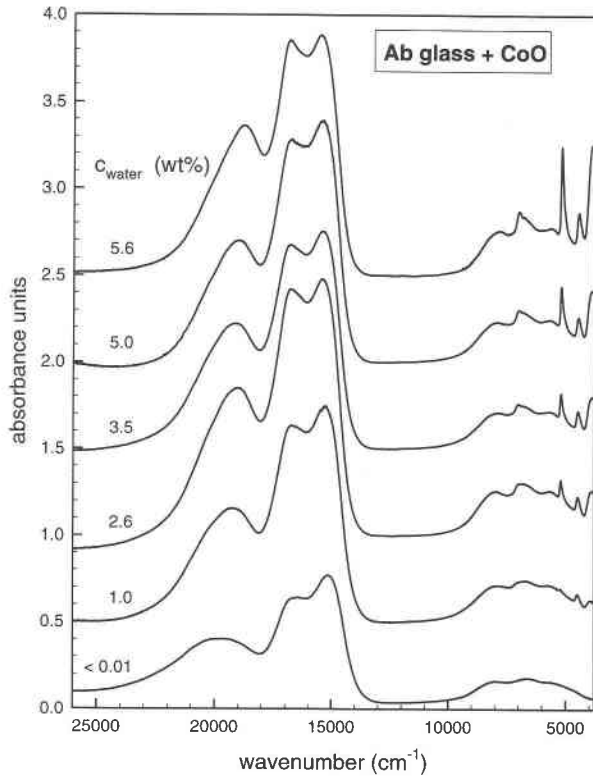


FIGURE 1. Absorption spectra of dry and hydrous CoO-doped albite (Ab) glasses normalized to 1 wt% CoO and 250 μm sample thickness.

were used. The high frequency spectra of the NiO-doped glasses ranging from 28000 to 37000 cm^{-1} were measured in one of the sample chambers of the spectrometer with a solar-blind-type Si diode detector.

Calculation of the glass transformation temperatures

According to Dingwell and Webb (1990) the glass transformation temperature of albite glass is about 1100 $^{\circ}\text{C}$ for an estimated quench rate of 200 $^{\circ}\text{C}/\text{s}$. The glass transformation temperature of hydrous albite melts depend strongly on the water content of the melt (Dingwell

TABLE 1. ICP-AES analyses of dry glass samples

	Ab05Ni02	Ab1Co00	Ideal albite
Composition in weight percent oxides			
SiO ₂	69.12	68.92	68.74
Al ₂ O ₃	18.64	18.54	19.44
Na ₂ O	11.79	11.59	11.82
NiO	0.45	<0.03	—
CoO	<0.01	0.95	—
CIPW norm (wt%)			
Qz	2.76	3.06	—
Ab	95.88	95.35	100
NaS	0.90	0.63	—

and Webb 1990; Nowak 1995; Hess 1996) and on the cooling rate (Dingwell and Webb 1990). We used the following equations to calculate the glass transition temperatures (Eq. 1: Hess 1996; Eq. 2: Scherer 1984):

$$\log \eta = [-3.545 + 0.833 \ln(w)] + [9601 - 2368 \ln(w)] \div \{T - [195.7 + 32.25 \ln(w)]\} \quad (1)$$

$$\log_{10} \eta = 11.3 - \log_{10} |q| \quad (2)$$

where η is the viscosity in Pa/s, w the water concentration in weight percent, T the temperature in K, and q is the quench rate in K/s.

RESULTS AND DISCUSSION

The chemical analyses of the dry CoO- and NiO-doped albitic glasses are given in Table 1. The experiment conditions, water contents, transition metal concentrations, and glass transition temperatures are compiled in Tables 2 and 3. The concentration-distance profiles of CoO and NiO of the hydrated samples show that the transition metals were homogeneously distributed in the glass blocks although some loss of Ni into the platinum capsule walls was observed.

The glass transition temperature of the quenched melts depends strongly on the water content. The transition temperatures range from 1100 $^{\circ}\text{C}$ for the dry albitic glass to 473 $^{\circ}\text{C}$ for an albitic glass containing 5.7 wt% water. The structure of the glass network probably corresponds more or less to the structure of the liquid at the glass

TABLE 2. Experiment parameters, water contents, CoO contents, and transition temperatures (T_g) of the CoO-doped albitic glasses

Sample no.	P (bar)	T ($^{\circ}\text{C}$)	t (h)	d (μm)	$C_{\text{water initial}}$ (wt%)	$C_{\text{OH, NIR}}$ (wt%)	$C_{\text{water, NIR}}$ (wt%)	ρ (g/L)	$C_{\text{CoO, ICP-AES}}$ (wt%)	T_g ($^{\circ}\text{C}$)
Ab1Co00	1	1000	1	228	—	—	<0.01 n.b.	2384	0.95	1100
		1300	4							
		1600	4							
WAb1Co01	2000	1015	120	264	4.93 (u)	1.70	4.98 n.b.	2315	0.69	492
WAb1Co05	500	1100	168	254	2.76 (s)	1.26	2.59 n.b.	2348	0.64	578
WAb1Co06	1000	1100	168	251	4.11 (s)	1.51	3.49 b.	2336	0.71	540
WAb1Co07	2000	1100	168	253	6.08 (s)	1.52	5.62 b.	2306	0.40	475
WAb1Co09	350	1165	24	241	1.02 (u)	0.85	1.03 b.	2370	0.72	685

Notes: d = thickness of the doubly polished glass plates; $C_{\text{water initial}}$ = water content inserted into the platinum capsules; $C_{\text{OH, NIR}}$, $C_{\text{water, NIR}}$ = concentration of OH and total water measured by near infrared spectroscopy; ρ = calculated density of the samples, for details see text; $C_{\text{CoO, ICP-AES}}$ = concentration of CoO measured with ICP-AES; T_g = calculated glass transition temperature, for details see text. (u) = water undersaturated; (s) = water saturated; b. = few bubbles; n.b. = no bubbles.

TABLE 3. Experiment parameters, water contents, NiO contents, and transition temperatures (T_g) of the NiO-doped albitic glasses

Sample no.	P (bar)	T (°C)	t (h)	d (μm)	$C_{\text{water initial}}$ (wt%)	$C_{\text{OH, NIR}}$ (wt%)	$C_{\text{water, NIR}}$ (wt%)	ρ (g/L)	$C_{\text{NiO, ICP}}$ (wt%)	T_g (°C)
Ab05Ni02	1	1000	1	498	—	—	<0.01 n.b.	2384	0.45	1100
		1300	3							
		1600	4							
WAb05Ni11	500	1100	120	504	2.73 (s)	1.43	2.57 b.	2349	0.11	579
WAb05Ni21	350	1164	24	509	0.99 (u)	0.82	1.08 n.b.	2369	0.30	680
WAb05Ni30	2000	1100	48	507	4.25 (u)	1.73	4.30 b.	2325	0.33	512
WAb05Ni33	2000	1070	48	507	3.68 (u)	1.65	3.69 n.b.	2333	0.30	533
WAb05Ni34	2000	1060	48	504	5.02 (u)	1.79	5.13 b.	2313	0.33	488
WAb05Ni37	2000	1100	48	1007	5.72 (u)	1.85	5.56 b.	2305	0.34	476
WAb05Ni38	2200	1100	48	1012	5.82 (u)	1.84	5.68 b.	2304	0.37	473

Note: For abbreviations see Table 2.

transformation temperature, although hydroxyl groups may recombine to molecular H₂O even below the glass transition (Nowak 1995; Nowak and Behrens 1995; Shen and Keppler 1995).

Co²⁺ in hydrous albite glass

The spectra of the dark blue dry and hydrous Co²⁺ doped albitic glasses are shown in Figure 1. The background-corrected ligand field spectrum of the dry glass (Fig. 2) consists of two triply splitted band systems: One strong band system in the VIS region around 16 600 cm⁻¹ and one weak band system in the NIR around 6600 cm⁻¹. This type of absorption spectrum is diagnostic for Co²⁺ in distorted tetrahedral coordination (Bamford 1962). According to Bamford (1962) the band system around 6600 cm⁻¹ can be attributed to the spin allowed transition ⁴A₂(F) → ⁴T₁(F) (ν_2). The three high frequency components can be assigned to one spin allowed ⁴A₂(F) →

⁴T₁(P) (ν_3) transition at around 16 600 cm⁻¹ and two spin forbidden transitions at about 15 100 cm⁻¹ [⁴A₂(F) → ²T₁(G)] and at 19 700 cm⁻¹ [⁴A₂(F) → ²T₂(G)] (Keppler 1992). Spectra of Co²⁺ tetrahedrally and octahedrally coordinated by O overlap somewhat around 20 000 cm⁻¹ (Wong and Angell 1976; Burns 1993; Keppler and Rubie 1993). Thus the glasses may contain a small amount of octahedrally coordinated Co²⁺. The proportion of octahedral Co²⁺ should be small because otherwise the extinction coefficients would decrease significantly below the values expected for tetrahedrally coordinated Co²⁺.

The spectra of the hydrous glasses up to 5.6 wt% water show strong changes in the NIR. These changes are due to the combination bands of (Si, Al)-OH and H₂O at 4500 and at 5230 cm⁻¹ and the first overtone of the fundamental OH stretching vibration of dissolved water at 7000 cm⁻¹. These bands overlap with the ⁴A₂(F) → ⁴T₁(F) (ν_2) transition. Subtle changes in the region from 10 000 to 25 000 cm⁻¹ occur in the shape of the electronic absorption spectra. An increase of water content from <0.01 to 1 wt% water leads to a decrease of the band intensity at about 15 100 cm⁻¹ relative to the two bands at higher frequencies (Fig. 1 and Table 4). This observation is consistent with the results of Keppler (1992), who showed that an increase of non-bridging O atoms in albite-diopside glasses affects the band system in the same way. The small change may be due to a change in the type of ligands around Co²⁺. Bridging and non-bridging O atoms coordinate Co²⁺ in dry albite glass. Presumably, mostly non-bridging O atoms coordinate Co²⁺ in the depolymerized albite-diopside glass. Another potential explanation for the increase of the high frequency component might be a change of a small fraction of Co²⁺ from tetrahedral to octahedral coordination.

Our observation that the environment of Co²⁺ in glasses is insensitive to the presence of water is consistent with previous studies of Co²⁺ in anhydrous sodium silicate glasses of variable composition (Bamford 1962; Nelson and White 1986). Over a wide range of compositions with very different degree of polymerization, the spectra of Co²⁺ are virtually unchanged. Apparently, Co²⁺ strongly favors a distorted tetrahedral environment.

Table 4 lists the observed band maxima and extinction

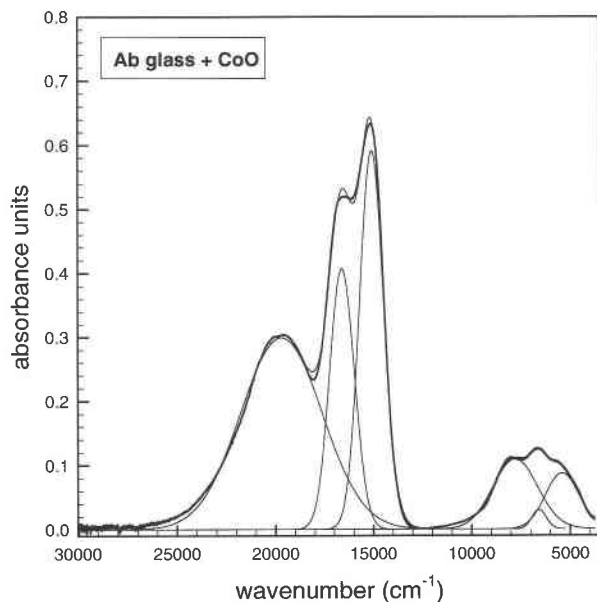


FIGURE 2. Background-corrected absorption spectrum of the dry CoO-doped albite (Ab) glass (Ab1Co00) deconvoluted with six Gaussian functions.

TABLE 4. Electronic absorption spectroscopic data of CoO-doped albite glasses

$c_{\text{water, NIR}}$ (wt%)	Ab1 Co00 <0.01		WAb1 Co09 1.03		WAb1 Co05 2.59		WAb1 Co06 3.49		WAb1 Co01 4.98		WAb1 Co07 5.62	
	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)	λ (cm ⁻¹)	ϵ (L·mol ⁻¹ ·cm ⁻¹)
	5401	12.6	5319	24.2	—	—	—	—	—	—	—	—
	6576	4.4	6638	10.0	—	—	—	—	—	—	—	—
	7774	15.8	7965	25.3	—	—	—	—	—	—	—	—
	15075	85.8	15209	148	15322	176	15304	147	15343	166	15434	160
	16589	59.1	16687	118	16726	140	16734	117	16742	137	16769	116
	19697	43.4	19342	80.5	19156	107	19231	87.1	19134	87.8	18835	98.6
10 Dq (cm ⁻¹)	3788		3822		(3800)*		(3800)*		(3800)*		(3800)*	
LFSE (kJ/mol)	36		37		(36)*		(36)*		(36)*		(36)*	
B (cm ⁻¹)	787		791		(796)*		(796)*		(797)*		(799)*	

Notes: λ = peak position, ϵ = extinction coefficient.

* These data are not very reliable, because of the difficulties to determine the barycenter of the ν_2 transition in the NIR of H₂O-bearing glasses.

coefficients from the deconvoluted spectra of the dry and hydrous CoO-doped albite glasses. The ligand field transition ${}^4A_2(F) \rightarrow {}^4T_2(P)$ (ν_1) is obscured by the fundamental stretching vibration of dissolved water. Thus the crystal field parameter $10Dq$ and the Racah parameter B were calculated from the Tanabe-Sugano matrices describing the ${}^4T_1(F)$ and ${}^4T_1(P)$ levels (König 1971):

$$10Dq = \frac{1}{34} \{9(\nu_2 + \nu_3) \pm [81(\nu_2^2 + \nu_3^2) - 178\nu_2\nu_3]^{1/2}\} \quad (3)$$

$$B = (\nu_2 + \nu_3 - 30Dq)15^{-1}. \quad (4)$$

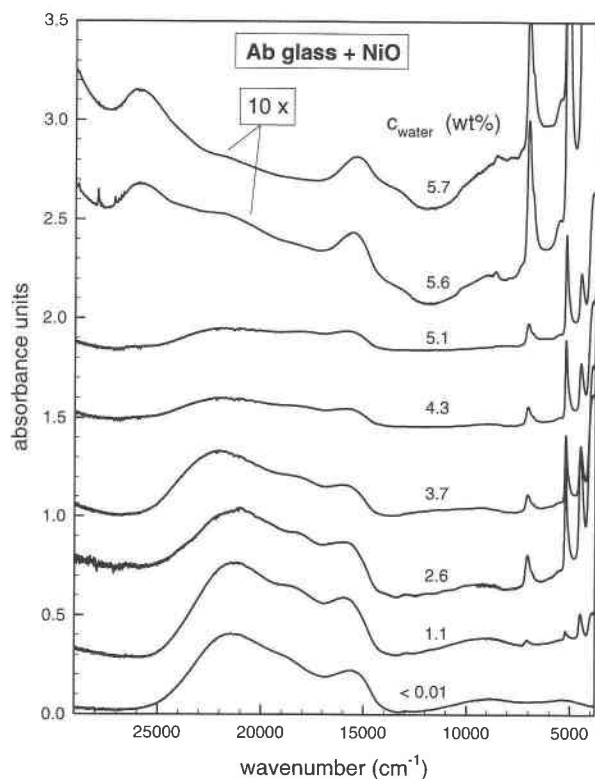


FIGURE 3. Absorption spectra of dry and hydrous NiO-doped albite (Ab) glasses normalized to 0.5 wt% NiO and 500 μm sample thickness.

The calculated values of $10Dq$, ligand field stabilization energy (LFSE), and Racah parameter B are listed in Table 4.

Ni²⁺ in hydrous albite glass

Anhydrous albite glass doped with NiO is brown. Below 5 wt% water, the color of the glasses remains constant. However, at about 5.6 wt% water, the color of the glasses abruptly changes from brown to light green, indicating a major change in the environment of Ni²⁺. The spectra of the Ni²⁺-doped glasses are shown in Figure 3.

The background corrected spectrum of the dry glass (Fig. 4) consists of two bands in the NIR-VIS region and of three bands in the VIS region, which can be attributed to Ni²⁺ in distorted octahedral coordination (Keppler 1992). The two low frequency absorption bands at 5160

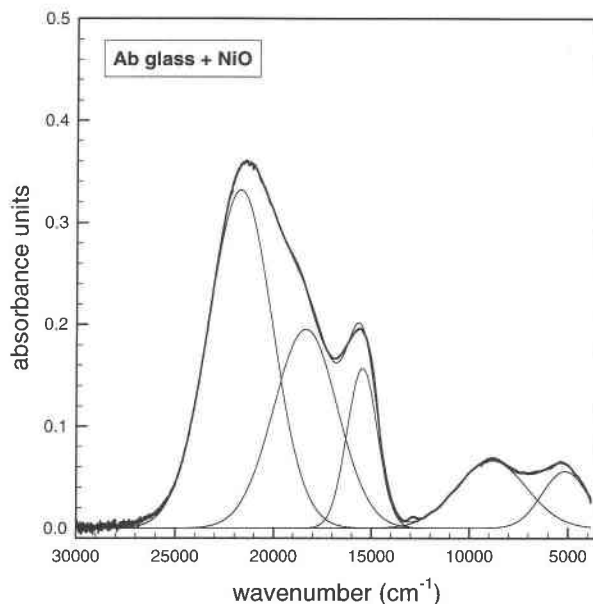


FIGURE 4. Background-corrected absorption spectrum of the dry NiO-doped albite (Ab) glass (Ab05Ni02) deconvoluted with five Gaussian functions.

TABLE 5. Electronic absorption spectroscopic data of NiO-doped albitic glasses

<i>c</i> _{water, NIR} (wt%)	Ab05Ni02 <0.01	WAb05Ni21 1.08	WAb05Ni11 2.57	WAb05Ni33 3.69	WAb05Ni30 4.30	WAb05Ni34 5.13	WAb05Ni37 5.56	WAb05Ni38 5.68
	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹	(L·mol ⁻¹) λ (cm ⁻¹)·cm ⁻¹
	5156 7.8	—	—	—	—	—	9000 n.d.	9000 n.d.
	8876 9.2	—	—	—	—	—	13300 n.d.	13400 n.d.
	15478 21.9	15627 26.4	15629 27.0	15719 12.6	15619 7.5	15606 8.0	15500 n.d.	15400 n.d.
	18380 27.3	18109 40.5	17495 22.9	18547 25.7	17776 9.8	17708 10.5	21800 n.d.	22000 v.w.
	21727 46.4	21643 58.6	21062 51.0	22354 39.8	21901 17.7	21844 14.0	25900 n.d.	26000 n.d.
10 <i>Dq</i> (cm ⁻¹)	5160	n.d.	n.d.	n.d.	n.d.	n.d.	9000	9000
LFSE (kJ/mol)	74	—	—	—	—	—	130	130
<i>B</i> (cm ⁻¹)	897	n.d.	n.d.	n.d.	n.d.	n.d.	918	918

Notes: n.d. = not determined; v.w. = very weak. λ = peak position. ε = extinction coefficient.

and at 8880 cm⁻¹ arise from the spin allowed transitions ³A_{2g}(F) → ³T_{2g}(F) (ν₁) and ³A_{2g}(F) → ³T_{1g}(F) (ν₂). The two high frequency bands at 18 380 and at 21 730 cm⁻¹ are caused by the ³A_{2g}(F) → ³T_{1g}(P) (ν₃) transition split through distortion of the coordination octahedra. The distinct band at 15 480 cm⁻¹ can be assigned to a spin forbidden transition ³A_{2g}(F) → ¹E_g(D) or to a small amount of tetrahedrally coordinated Ni²⁺ (Bamford 1962; Burns and Fyfe 1964). Spectra of hydrated glasses with up to 5.7 wt% water show strong changes in the NIR region because of the combination bands of T-OH and H₂O. However, below 5.1 wt% water content only minor changes occur in the electronic absorption spectrum of Ni²⁺. Ligand field parameters of the dry glass (10 *Dq* = 5160 cm⁻¹, *B* = 897 cm⁻¹) were calculated using equa-

tions for octahedral *d*⁸ configuration given by König (1971):

$$10Dq = \nu_1 \quad (5)$$

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15. \quad (6)$$

and the band positions of the background corrected and deconvoluted spectrum (Fig. 4 and Table 5).

The electronic absorption spectra of the green-colored glasses containing 5.6 and 5.7 wt% water differ from the other spectra (Fig. 3) but resemble spectra of an aqueous 0.1 molar NiCl₂ solution, where Ni²⁺ is in regular octahedral coordination (Fig. 5). Three absorption bands can be distinguished. One band occurs at about 9000 cm⁻¹, another occurs at 15 400 with a shoulder at 13 400 cm⁻¹, and a strong absorption band exists at 26 000 cm⁻¹ (Fig. 5). The glass with 5.6 wt% water shows also a weak absorption at 21 800 cm⁻¹ that is due to a small amount of Ni²⁺ remaining in a distorted octahedral site. This feature disappears almost completely at a water content of 5.7 wt%. The absorption band at 9000 cm⁻¹ can be assigned to the ³A_{2g}(F) → ³T_{2g}(F) (ν₁) transition, the distinct shoulder at about 13 400 cm⁻¹ can be attributed to the ³A_{2g}(F) → ³T_{1g}(F) (ν₂) transition and the high frequency band at 26 000 cm⁻¹ to the ³A_{2g}(F) → ³T_{1g}(P) (ν₃) transition because of Ni²⁺ in a regular octahedral field. The band at 15 400 cm⁻¹ can be attributed to the spin forbidden transition ³A_{2g}(F) → ¹E_g(D) of octahedral Ni²⁺ or to an absorption because of small amounts of tetrahedrally coordinated Ni²⁺.

The equations

$$10Dq = \nu_1 \quad (7)$$

$$B = (2\nu_2^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1) \quad (8)$$

of König (1971) give the ligand field parameters 10 *Dq* = 9000 cm⁻¹ and *B* = 918 cm⁻¹ (Table 5).

The close similarity of the spectrum of the glass to 5.7 wt% water to the spectrum of hydrous Ni²⁺-solutions suggests a very similar environment of Ni²⁺ in both phases. In hydrous solutions, the Ni²⁺-hexaquoocomplex is usually the dominant species of Ni²⁺. It is therefore likely that in the water-rich glasses, Ni²⁺ is also surrounded by six H₂O

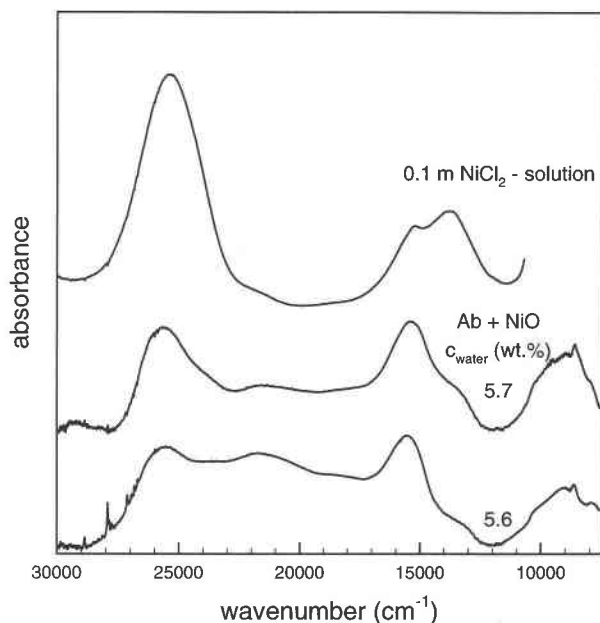


FIGURE 5. Absorption spectra of the hydrated NiO-doped albitic (Ab) glasses containing 5.6 (WAb05Ni37) and 5.7 wt% H₂O (WAb05Ni38) and a 0.1 m NiCl₂ solution (path length = 10 mm). The spectra were scaled for comparison.

molecules in perfect octahedral coordination. This could be an artifact if submicroscopic fluid inclusions were present in the glass. However, the glass is optically clear and even if some Ni²⁺ were present in submicroscopic inclusions, this scenario would not explain the disappearance of the spectrum of Ni²⁺ in distorted octahedral coordination. Moreover, analysis of the water speciation, i.e., the equilibrium between OH and molecular H₂O in the glass with 5.8 wt% water does not reveal any anomalies that suggest the presence of a second phase in the glass.

The formation of a hexaquo complex in the glass also offers an elegant explanation for the abrupt change of speciation at a certain water content. At water concentrations above about 4 wt%, additional water is essentially incorporated in albite glass as molecular H₂O (Silver and Stolper, 1989), implying that the H₂O concentration increases steeply with total water content. The equilibrium between Ni²⁺ coordinated by O atoms not belonging to molecular H₂O and the Ni²⁺ hexaquo complex can be described by the equation



with the equilibrium constant

$$K = \frac{[\text{Ni}(\text{H}_2\text{O})_6][\text{O}]^6}{[\text{NiO}_6][\text{H}_2\text{O}]^6} \quad (10)$$

This equation predicts an increase of the concentration of the hexaquo complex in the glass with the sixth power of H₂O concentration. Accordingly, it is not surprising that this speciation change occurs sharply at a certain water content. The abrupt change in the coordination environment of Ni²⁺ in hydrous glasses is very similar to what is observed in many salt-water systems. It has been shown by IR spectroscopy and other techniques (Valyashko 1977) that upon addition of water to a salt melt, the coordination sphere of the cations changes abruptly at a certain water concentration from a "melt-like" to a "fluid-like" regime.

Close inspection of Figure 3 indicates some anomalies in the spectra already exist at 4.3 and 5.1 wt% water. These spectra show an anomalously low absorbance in the high-frequency region. Because extinction coefficients of crystal field bands are greatly enhanced by distortion, this low absorbance may indicate a decreasing distortion of the octahedron around Ni²⁺, possibly because of the depolymerization of the glass that reduces steric constraints.

The ligand field splitting and LFSE of the Ni hexaquo complex in the water-rich glasses is much higher than for Ni²⁺ in the distorted octahedral site of the low water content glasses. Although the interpretation of the spectra of the water-rich glass is very straightforward, the incorporation mechanism of Ni²⁺ in anhydrous silicate glasses has been the subject of considerable debate. Galois and Calas (1993) suggested, largely based on extended X-ray absorption fine structure spectroscopy (EXAFS) data, that Ni²⁺ in silicate glasses is mostly in a fivefold-coordinated

site rather than in a distorted octahedral environment. However, both theoretical calculations of crystal field spectra and spectroscopic measurements of crystalline compounds containing fivefold-coordinated Ni²⁺ (Ciampolini 1966; Morassi et al. 1973) always show three bands in the near infrared range, whereas we only observe two bands of perfect Gaussian shape (Fig. 4). Accordingly, our preferred interpretation of the spectra of the low water content glasses is based on a model with Ni²⁺ in distorted octahedral coordination. However, it should be emphasized that the major new observation of this study, a radical change in the environment of Ni²⁺ in glasses with high water content, is of course independent of the details of band assignments.

GEOLOGICAL APPLICATIONS

The effect of water on the environment of network-modifying cations that we observe for Ni²⁺ appears to occur in other systems as well. In an EXAFS study of Mn-bearing glasses, Kohn et al. (1990) found that Mn²⁺ in hydrous glasses is in regular octahedral coordination, although the effective coordination number of Mn²⁺ appeared to be smaller in anhydrous systems. Similarly, it has been suggested that the presence of water strongly affects the environment of alkali ions in glasses (Kohn et al. 1989). Whether such effects also occur in silicate melts under geologically relevant conditions of *P-T* and water content remains to be studied by in-situ spectroscopic experiments. On the basis of the information available from glasses, it is reasonable to expect that water changes the environment of some network-modifying cations drastically and that the change may occur sharply at a certain water content.

For Ni²⁺, it is relatively easy to estimate how the partitioning between minerals, melts, and a metal phase could change in the presence of water. Ni²⁺ is an ion with a very large LFSE. It has been shown that the partitioning of such ions can often be quantitatively predicted by considerations of LFSE (Calas and Petiau 1983; Keppler 1992). This partitioning implies that the free energy of the exchange reaction of Ni²⁺, e.g., between silicate melts and minerals, is essentially determined by the differences in LFSE. According to the measured LFSE of Ni²⁺ in dry and hydrous albite glass, the mineral-melt and metal-melt partition coefficients should decrease by one to two orders of magnitude at 1100 °C once the water content raises above a critical value. In some cases this would be sufficient to convert Ni from a compatible into a slightly incompatible element during magmatic fractionation. Similarly, a sufficiently high water content could decrease metal-silicate melt partition coefficients significantly and thereby reduce the siderophilic nature of Ni. Understanding the influence of water on the distribution of trace elements in magmatic systems requires much additional experimental work. In particular, one cannot assume that if small amounts of water have a negligible effect on partition coefficients, this will also hold true for water contents in the range of 5–10 wt% or above. High

water contents are realistic for some magmas generated in subduction zones as well as for late-stage granitic pegmatites.

Shen and Keppler (1997) recently demonstrated that the miscibility gap between albite melt and hydrous fluid disappears beyond the critical curve going through the points 989 °C, 10.6 kbar and 623 °C, 16.5 kbar. This implies that the structure of albite melt can change continuously with increasing water content, until it reaches the structural state of a dilute hydrous solution. It is obvious that the formation of a hydration shell around network modifying cations, as we observed it for Ni²⁺, leads to a structure intermediate between a silicate melt and a hydrous fluid. Therefore, the occurrence of such an effect in hydrous silicate melts may be directly related to the onset of critical behavior.

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