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The aqueous geochemistry of gallium, germanium, indium and scandium

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Abstract

Relatively little information is available in the literature regarding the speciation and solubility of Ga, Ge, In and Sc in aqueous solutions, especially at elevated temperatures and pressures. In this paper we critically review stability constants for relevant aqueous complexes of these metals and solubility products for relevant solid phases. Most of the available data refer to standard conditions of temperature and pressure (25 °C and 1 bar), although for Ga and Ge, experimentally derived data are available for some geologically relevant species and phases up to 200–300 °C. The stable oxidation states of the four metals in aqueous solution are Ga(III), Ge(IV), In(III) and Sc(III). The ions of each of these metals are relatively hard in the Pearson [Pearson, R.G. 1963. Hard and soft acids and bases. Journal of the American Chemical Society 85, 3533–3539] sense, forming the strongest complexes with hard ligands such as hydroxide, fluoride, sulfate and phosphate, and weaker complexes with soft ligands such as chloride and bisulfide. The main exception to this rule is In(III), which forms reasonably stable chloride and bisulfide complexes. The hydrated Ga^{3+}, In^{3+} and Sc^{3+} ions are all octahedrally coordinated by water molecules, but there is some evidence, e.g., for $GaCl_4^-$ and $InCl_4^-$, that a conversion to tetrahedral coordination may occur upon replacement of water by a sufficient number of other ligands.

In most hydrothermal solutions, we predict that hydroxide complexes will be the most important forms of transport of Ga and Sc, although fluoride complexes will be important in environments where fluoride activities are relatively high (e.g., during greisen formation). In analogy with Si, the most important species for Ge is germanic acid, $H_4GeO_4^0$, but again fluoride complexes may be important at high fluoride activities. Chloride complexes are not expected to play a significant role in the transport of Ga, Ge or Sc at temperatures below approximately 300 °C. The behavior of In is expected to be the most variable, with, depending on conditions, hydroxide, chloride, fluoride or bisulfide complexes all contributing to its transport. Sulfate and phosphate complexes of Ga, In and Sc may play limited roles in the hydrothermal mass transfer of these elements, but only under special conditions; normally these complexes will be less important than hydroxide or fluoride complexes.

Solubility calculations for 25 °C indicate that In-sulfide and Sc-phosphate are less soluble (i.e., more stable) than the corresponding oxyhydroxides, even when In-bisulfide and Sc–phosphate complexes are taken into account. However, the phases $GaPO_4$(s) and $InPO_4$(s) are generally more soluble than the corresponding oxyhydroxides. Solubilities of α-GaOOH(s) and GeO_2(tetragonal) have been estimated up to 300 °C and both increase with increasing temperature. The solubility of pure α-GaOOH(s) at 25 °C ($<10^{-6}$ m) is quite low from pH 3 to pH 8, consistent with the general immobility of Ga in the weathering environment and its concentration in bauxites.

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1. Introduction

Gallium, germanium, indium and scandium are relatively rare elements of strategic importance. They are employed in a variety of high-technology applications such as integrated circuits, optoelectronic devices, fiber optics, thin-film coatings, and metal alloys. Because of their scarcity in most geological environments, minerals containing these elements as essential components are exceedingly rare. These four elements are far more commonly found as minor substituents in more common minerals, a fact that complicates thermodynamic modeling of the solubilities of these metals in aqueous solutions. For example, in the Apex Ga–Ge deposit, Utah, Ga and Ge have been found to occur predominantly in jarosite and goethite/hematite, respectively (Dutrizac et al., 1986; Bernstein and Waychunas, 1987). Owing to similarities in ionic radii, Ga^{3+} frequently substitutes for Al^{3+} and/or Fe^{3+} in common rock-forming minerals (Burton and Culkin, 1978). Germanium follows Si^{4+} and Fe^{3+} in oxides and silicates, but is also (as is Ga) enriched in sulfide minerals such as sphalerite, galena, enargite, luzonite and bornite (Hörmann, 1978). The independent Ga-bearing minerals, gallite [$CuGaS_2$] and söhngeite [$Ga(OH)_3$], and Ge-bearing minerals, argyrodite [Ag_8GeS_6], germanite [$Cu_{13}Fe_2Ge_2S_{16}$], renierite [$(Cu,Zn)_{11}(Ge,As)_2Fe_4S_{16}$], briartite [$Cu_2(Fe,Zn)GeS_4$], stottite [$Fe^{2+}Ge(OH)_6$], fleischerite [$Pb_3Ge(SO_4)_2(OH)_6 \cdot 3H_2O$], itoite [$Pb_3Ge(SO_4)_2O_2(OH)_2$], schaurteite [$Ca_3Ge(SO_4)_2(OH)_6 \cdot 3H_2O$], brunogeierite [$GeFe_2O_4$], carboirite [$Fe(Al,Ga)_2O(Ge,Si)O_4(OH)_2$], and argutite [$GeO_2$] are quite rare (Ottemann and Nuber, 1972; Burton and Culkin, 1978; Hörmann, 1978; Wang, 1978; Johan et al., 1983). According to Bernhard et al. (1998), only six minerals in which Sc is a major constituent currently are known: thortveitite [$(Sc,Y)_2Si_2O_7$], bazzite [$Be_3(Sc,Al)_2Si_6O_{18}$], cascandite [$Ca(Sc,Fe^{2+})Si_3O_8(OH)$], jervisite [$(Na,Ca,Fe^{2+})(Sc,Mg,Fe^{2+})Si_2O_6$], kolbeckite [$ScPO_4 \cdot 2H_2O$], and pretulite [$ScPO_4$]. However, the minerals juonnite [$CaMgSc(PO_4)_2OH \cdot 4H_2O$] (Liferovich and Gogol, 1999) and kristiansenite, $Ca_2ScSn(Si_2O_7)(Si_2O_6OH)$ (Raade et al., 2002) should also be added to this list. Rare In minerals include dzhalindite [$In(OH)_3$], indite [$Fe^{2+}In_2S_4$] and roquesite [$CuInS_2$] (Linn and Schmitt, 1974), laforetite [$AgInS_2$] and $(Zn,Fe)_2Cu_3In_3S_8$ (Cantinolle et al., 1985; Meisser et al., 1999), and yanomamite [$InAsO_4 \cdot 2H_2O$] (Botelho et al., 1994). Indium is commonly enriched in sulfide minerals such as sphalerite, stannite and chalcopyrite, and also in the tin oxide, cassiterite (Linn and Schmitt, 1974).

These elements are exclusively produced as by-products of the mining of other commodities, increasing the potential value of the latter (Geldron, 1983): Ga from bauxite ores; Ga, Ge, and In from Zn and Pb–Zn–Cu sulfide ores; In from cassiterite ores; and Sc from a variety of ore types, including those of U. In spite of the importance of hydrothermal and weathering processes in generating ores from which Ga, Ge, In and Sc are extracted, very little is known about the aqueous geochemistry of these elements, especially at elevated temperatures and pressures. In particular, solubilities of relevant minerals, and stoichiometries and stabilities of aqueous complexes containing these elements at conditions relevant to hydrothermal and supergene ore formation have received relatively little attention. In this paper, available data are critically reviewed and synthesized, and it is hoped that this paper will stimulate and guide future experiments to provide additional information on these elements.

2. General aqueous chemistry of Ga, Ge, In and Sc

In what follows, we employ the following convention regarding notation for oxidation states of cations. When referring to the simple, hydrated metal ion we write M^{q+}, where q represents the ionic charge. However, when referring to the general oxidation state of a metal, we write $M(Q)$, with Q being the oxidation state in uppercase Roman numerals. Thus, the simple hydrated trivalent gallium ion is written Ga^{3+}, but we refer to trivalent Ga–chloride complexes as Ga(III)–chloride complexes.

The only stable oxidation states of these elements in aqueous solution are III for Ga, In and Sc, and IV for Ge. The radii of these ions are compared in Table 1, from which it can be seen that Ga^{3+}, In^{3+} and Sc^{3+} are all somewhat larger than Al^{3+}, and that Ge^{4+} is somewhat larger than Si^{4+}. The high charge and moderate size of these ions dictates that they are "hard" acids in the sense of Pearson (1963) (see also Wood and Samson, 1998), and should prefer to form complexes with hard bases such as OH^-, F^- and organic ligands bonding through oxygen, e.g., acetate. Conversely, complexes of these metals with soft bases, such as HS^-,

Table 1
Ionic radii for the ions of interest

Ion	Radius (Å)	Ion	Radius (Å)
Al^{3+}	0.54[1]	In^{3+}	0.80[1]
Ga^{3+}	0.62[1]	Sc^{3+}	0.75[1]
Ge^{4+}	0.39[2]	Si^{4+}	0.26[2]

[1]Octahedral coordination; [2]Tetrahedral coordination.
From Shannon (1976) as quoted by Henderson (1982).

are not expected to be geochemically important, with the exception of In^{3+}. The Sc^{3+} ion contains no *d*-electrons, but Ga^{3+}, $Ge^{4+}$and In^{3+}each contain a full complement of 10 *d*-electrons in their valence shells, leading to a greater degree of covalent bonding (i.e., greater softness) in complexes of the latter three ions compared to Al^{3+}, Sc^{3+} and Si^{4+}. This greater tendency towards covalent bonding results in a greater tendency of Ga^{3+}, Ge^{4+} and In^{3+} to form stable chloride complexes. In fact, the tendency to form chloride complexes increases substantially as one proceeds down the series $Al^{3+} \rightarrow Ga^{3+} \rightarrow In^{3+}$. Because all these ions contain either completely empty (Sc^{3+}) or completely full (Ga^{3+}, Ge^{4+} and In^{3+}) d-orbitals, ligand-field effects (cf. Crerar et al., 1985) play no role in their chemistry.

3. Concentrations of Ga, Ge, In and Sc in geothermal waters

Analytical data for waters from active geothermal systems provide important information on the likely concentrations of metals in fossil hydrothermal systems. Table 2 summarizes information available in the literature on the concentrations of Ga and Ge in continental and oceanic geothermal systems. Data for In and Sc could not be found.

There are more data available on concentrations in geothermal fluids for Ge than for Ga. The concentrations of these metals are generally low, with reported values ranging from 0.1 to 72 ppb for Ga, and <0.5 to 130 ppb for Ge. For the most part, the geothermal fluids listed in Table 2 are relatively dilute, have pH values that are slightly acidic to near neutral, and do not contain unusually high concentrations of ligands that form strong complexes with Ga and Ge, such as F^-. Thus, we can conclude that, in hydrothermal systems that do not contain strong ligands for these metals, their concentrations probably will be less than 1 ppm. The importance of ligand identity and concentration is illustrated by data on warm (up to 60 °C) carbonate waters from the Pamirs in Russia (Kraynov, 1967) in which Ge concentration was very strongly correlated with the fluoride content, and to a lesser extent with the emergence temperature of the spring. The data available are clearly limited, and it can therefore be expected that certain combinations of fluid composition and temperature exist for which the concentrations of these metals are much higher. Indeed, the existence of hydrothermal enrichments of these metals demands that such conditions exist. For example, both Ge (up to 100 ppm) and Ga (up to 700 ppm) are known to occur in precipitates from active geothermal systems (Weissberg et al., 1979; Krupp and Seward, 1987).

Table 2
Measured concentrations of Ga and Ge in thermal waters

Location	No. of samples	Concentration (ppb)*	Reference
Gallium			
Japan	98	2.5 (0.11–72)	Uzumasa and Nasu (1960)
Bath, England	1	0.63	Riley (1961)
Wairakei, New Zealand	1	~0.2	Goguel (1988)
Broadlands, New Zealand	1	~0.6	Goguel (1988)
Germanium			
Beppu, Japan	12	12	Kawakami et al. (1956)
Japan	129	11.0 (0.4–43.8)	Uzumasa et al. (1959)
Misasa, Japan	22	(2–20)	Sakanoue (1960)
Bulgaria		(X–X0)	Pentcheva (1964)
USSR		(<2–90)	Kraynov (1965, 1967)
TVZ, New Zealand	37	46 (0–128)	Koga (1967)
Iceland	132	(<0.5–53)	Arnórsson (1984)
Vals les Bains, France	17	16.4 (0.5–48)	Criaud and Fouillac (1986)
Vichy, France	18	12.5 (2.0–20)	Criaud and Fouillac (1986)
Wairakei, New Zealand	1	~6	Goguel (1988)
Broadlands, New Zealand	1	~3	Goguel (1988)
21°N East Pacific Rise		(9.4–12.3)	Mortlock et al. (1993)
Juan de Fuca Ridge		(10.9–18.9)	Mortlock et al. (1993)

* Mean values given with range in parentheses.

Although there are no data on In concentrations in geothermal waters, Nozaki et al. (2000a,b) have recently published data on In concentrations in rivers and estuaries which provide some constraints on the levels of this metal likely to be encountered in natural waters. In Japanese river/estuary systems thought to be affected by anthropogenic inputs of indium, the concentrations ranged from 1 to 14.7 pmol kg^{-1} (0.1 to 1.7 parts per trillion), with concentrations decreasing as seawater becomes mixed with river water. In the Chao Phraya River in Thailand, indium concentrations were even lower, at 0.03 to 0.4 pmol kg^{-1} (0.003 to 0.05 parts per trillion). These data hint that the concentration of indium in many natural waters may be extremely low. However, as with Ga and Ge, the existence of hydrothermal enrichments of In and Sc indicates that there must exist certain conditions under which these elements are relatively soluble. As an example, Schwarz-Schampera and Herzig (1997) reported In contents up to 590 ppm in polymetallic sulfides from the Valu Fa Ridge in the Pacific Ocean.

4. Review of data on metal complexes

In this section we critically review available data on the composition and thermodynamics of geologically relevant inorganic complexes of Ga, Ge, In and Sc. The ligands dealt with in this study are hydroxide, fluoride, chloride, sulfate, bisulfide, and phosphate. We were unable to find any references dealing with carbonate or bicarbonate complexes of these metals, but it should be noted that such complexes could be of potential importance, especially for Sc. Although complexes of Ga, Ge, In and Sc with organic ligands (e.g., acetate, oxalate, humic and fulvic acids) could play a role in their mass transport, particularly at lower temperatures, such complexes were deemed outside the scope of this paper. Where possible, for each of the metals and ligands considered, we provide recommended values of the stability constants at infinite dilution. The majority of the data available are conditional stability constants valid at a specific ionic strength. Thus, in many cases, extrapolation to infinite dilution was required as described below. In discussing hydrolysis, we rely heavily on the critical review of Baes and Mesmer (1986) in assessing data published prior to circa 1974 (Baes and Mesmer was originally published in 1976, but was reprinted without revision in 1986).

4.1. Notation

The general reaction for the hydrolysis of a trivalent cation can be written:

$$pM^{3+} + qH_2O(l) \leftrightarrow M_p(OH)_q^{3p-q} + qH^+. \quad (1)$$

The equilibrium constant for this reaction is given the symbol K_{hpq} and is defined as:

$$K_{hpq} = \frac{a_{H^+}^q a_{M_p(OH)_q^{3p-q}}}{a_{M^{3+}}^p a_{H_2O}^q}. \quad (2)$$

Similarly, the general reaction for the complexation of a trivalent cation with any ligand L may be expressed as:

$$M^{3+} + nL^{-z} \leftrightarrow ML_n^{3-nz}. \quad (3)$$

For which the cumulative stability constant is defined as:

$$\beta_n = \frac{a_{ML_n^{3-nz}}}{a_{M^{3+}} a_{L^{-z}}^n}. \quad (4)$$

4.2. Extrapolation of equilibrium constants to infinite dilution

For systems where sufficient reliable equilibrium constant data were available over an adequate range of ionic strength, we performed an empirical extrapolation to infinite dilution. This extrapolation was accomplished using the following expression:

$$\log K^I = \log K^0 + \frac{A\Delta Z^2\sqrt{I}}{1+\sqrt{I}} + CI \quad (5)$$

where K^I is the conditional equilibrium constant at ionic strength I, K^0 is the equilibrium constant at infinite dilution, ΔZ^2 is the change in charges squared for the reaction, A is the Debye–Hückel parameter and C is an adjustable parameter. This is essentially the same equation employed by Baes and Mesmer (1986) to extrapolate hydrolysis constants to infinite dilution in their critical review. The values of log K^0 and C were determined via regression analysis of the data deemed to be reliable. Regression was accomplished using the least-squares routine in the software package SigmaPlot® (Jandel Scientific), which employs the Marquardt–Levenberg algorithm.

4.3. Gallium

According to NMR and EXAFS studies, the coordination number of the hydrated Ga^{3+} ion is 6 (Fiat and Connick, 1966; Swift et al., 1967; Muñoz-Páez et al., 1997; Lindqvist-Reis et al., 1998). On the other hand, the gallate ion, $Ga(OH)_4^-$, may have tetrahedral coordination, in analogy with $Al(OH)_4^-$, although the geometry of the latter is still somewhat controversial (Akitt and Gessner, 1984). Moreover, based on Raman spectroscopic measurements, Woodward and Nord (1956) deduced that the $GaCl_4^-$ ion exhibits tetrahedral coordination.

4.3.1. Hydroxide complexes

A number of studies of gallium hydrolysis have been conducted, many of which were reviewed by Baes and Mesmer (1986). The hydrolysis constants for the monomeric Ga hydroxide species obtained in these various studies are summarized in Table 3 and depicted in Fig. 1. Baes and Mesmer (1986) point out that, because Ga^{3+} is prone to form polynuclear hydroxide species (e.g., $Ga_{26}(OH)_{65}^{13+}$) at Ga concentrations required for accurate measurement using most experimental techniques (potentiometry, spectroscopy), equilibrium constants for the formation of monomeric Ga(III)–

Table 3
Summary of Ga^{3+} hydrolysis constants from the literature

Medium	Temperature (°C)	log K_{hpq}				
		$GaOH^{2+}$	$Ga(OH)_2^+$	$Ga(OH)_3^0$	$Ga(OH)_4^-$	Source
0.05 M GaX_3	25	−3.17	–	–	–	50MK
0.02 M GaX_3	25	−3.00	–	–	–	50MK
0.01 M GaX_3	25	−2.90	–	–	–	50MK
0	25	−2.6	–	–	–	50MK
0	25	–	–	−9.8	−16.6	57F/62I
1 M $NaClO_4$	25	<−2.7	–	–	–	59RT
0?	25	–	–	–	−17.3	67VL
3 M KCl	25	<−4.3	–	–	–	67HC
3 m $NaClO_4$	60	<−3.8	–	–	–	67GS
0.1 M NaCl	25	−2.9	−6.6	−11.0	–	68N
≤0.0005 M	25	−4.2	–	–	–	70H
0.1 M $NaClO_4$	25	−2.87	−6.55	−11.07	–	73BN
0.3 M $NaClO_4$	25	−2.48	−5.67	−9.69	–	73BN
0.5 M $NaClO_4$	25	−2.30	−5.20	−8.64	–	73BN
1.0 M $NaClO_4$	25	−1.78	−3.88	−6.16	–	73BN
?	25?	−3.28	–	–	–	76N
0.5 M KNO_3	25	−2.46	–	−8.2	−17.3	84T
0.5 M $NaClO_4$	10	−4.17	−8.21	–	–	85CT
0	25	−3.46	−7.70	–	–	85CT
0.1 M $NaClO_4$	25	−3.50	−7.67	–	–	85CT
0.5 M $NaClO_4$	25	−3.69	−7.43	–	–	85CT
1.5 M $NaClO_4$	25	−4.15	−6.97	–	–	85CT
0	25	−2.6	−5.9	−10.3	−16.6	86BM
0	25	−2.56	−6.07	–	–	89B
0.1 M KNO_3	25	−3.16	−7.07	–	–	89B
0.5 M KNO_3	25	−3.73	−7.15	–	–	89B
1.0 M KNO_3	25	−3.92	−7.79	–	–	89B
1.5 M KNO_3	25	−4.02	−7.73	–	–	89B
0.1 M $NaNO_3$	25	−3.15	–	–	–	91D
0	25	–	–	–	−15.66	97D
0	150	−1.83	−3.55	−6.75	−10.45	97B
0	25	−2.85	−7.28	−11.94	–	97B*
1 m NaCl	25	−3.78	–	–	–	98UO
1 m NaCl	50	−3.33	–	–	–	98UO
1 m NaCl	75	−2.96	–	–	–	98UO
1 m NaCl	100	−2.38	–	–	–	98UO
0	25	−2.85	–	–	–	98UO
0	50	−2.36	–	–	–	98UO
0	75	−1.98	–	–	–	98UO
0	100	−1.45	–	–	–	98UO

Sources: 50MK—from data of Moeller and King (1950); 57F/62I—from data of Fetter (1957) and Ivanov-Emin et al. (1962); 58RT—from data of Ruff and Tyree (1958); 67VL—calculated by Vagramjan and Leshawa (1967); 67HC—from data of Haladjian and Carpéni (1967); 67GS—from data of Gamsjäger and Schindler (1967); 68N—Nazarenko et al. (1968); 70H—Hemmes et al. (1970); 73BN—Biryuk and Nazarenko (1973); 76N—Nishida (1976); 84T—Tóth et al. (1984); 85CT—Campisi and Tregloan (1985); 86BM—recommended values from critical review by Baes and Mesmer (1986); 89B—Brown (1989); 91D—Duma et al. (1991); 97D—Diakonov et al. (1997); 97B—Bénézeth et al. (1997); 97B*—extrapolated to 25 °C by Bénézeth et al. (1997) based on their data at 150 °C; 98UO—Uchida and Okuwaki (1998).

hydroxide complexes (such as $GaOH^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3^0$ and $Ga(OH)_4^-$) are difficult to measure and are therefore comparatively poorly known.

The measurements of K_{h11} for $GaOH^{2+}$ show a significant amount of disagreement (Fig. 1a). The results of Campisi and Tregloan (1985) and Hemmes et al. (1970) at infinite dilution appear to be too low compared to the bulk of the data. On the other hand, the results of Biryuk and Nazarenko (1973), and Tóth et al. (1984) appear to be too high compared to the remaining data. Moreover, the trend of the data of Biryuk and Nazarenko (1973) with respect to ionic strength is contrary to that expected from the form of Eq. (5). Assuming that the data of Moeller and King (1950) and Nazarenko et al. (1968), which Baes and Mesmer (1986) employed to derive their fit to Eq. (5), are

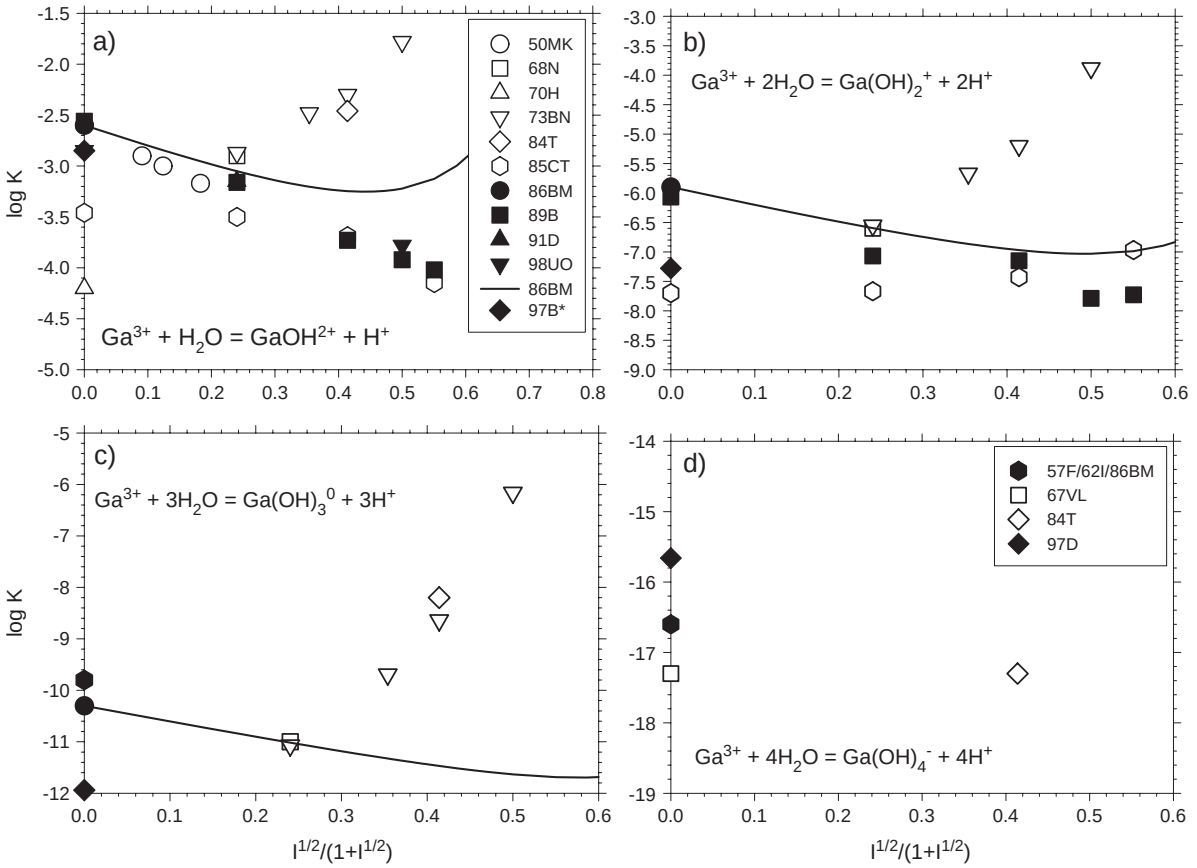

Fig. 1. Literature values of the hydrolysis constants for the species: (a) $GaOH^{2+}$; (b) $Ga(OH)_2^+$; (c) $Ga(OH)_3^0$ and (d) $Ga(OH)_4^-$ vs. $I^{½}/(1+I^{½})$, where I is ionic strength. The data are for 25 °C. Details regarding the sources of the data are given in the footnote to Table 3. The solid curves represent values calculated using the equation provided by Baes and Mesmer (1986) that has the form of Eq. (5) and was based the data of Moeller and King (1950) and Nazarenko et al. (1968).

correct, then the data of Biryuk and Nazarenko (1973) and Tóth et al. (1984) increase too sharply with ionic strength. In addition, the results of the study of Brown (1989) lie along a trend that is more consistent with the data at lower ionic strength. Finally, in their critical review of the available data, Bénézeth et al. (1997) also rejected the data of Biryuk and Nazarenko (1973). Bénézeth et al. (1997) determined log K_{h11} at 150 °C and then extrapolated this value to lower and higher temperatures within the framework of the modified-Helgeson–Kirkham–Flowers (HKF) equation (Helgeson et al., 1981; Shock and Helgeson, 1988; Tanger and Helgeson, 1988). Their extrapolated value is within 0.3 log units of the value recommended by Baes and Mesmer (1986), and is essentially identical to that recently determined by Uchida and Okuwaki (1998). Furthermore, the HKF-equation parameters of Bénézeth et al. (1997) permit calculation of log K_{h11} over a range of temperatures and pressures. Therefore, we adopt their estimates in this paper.

For $Ga(OH)_2^+$, $Ga(OH)_3^0$, and $Ga(OH)_4^-$ the data are also scattered (Fig. 1b–d). Bénézeth et al. (1997) obtained hydrolysis constants for these species at 25 °C by extrapolation of their results at 150 °C using the HKF equation. Fig. 1b, c, and d show that the values obtained by Bénézeth et al. (1997) differ considerably from the values recommended by Baes and Mesmer (1986). The reasons for this discrepancy are not clear. For the time being, we favor the values given by Bénézeth et al. (1997) for the following reasons. First, we can find no flaws in their experimental approach, and for $GaOH^{2+}$, the agreement between values given by Baes and Mesmer (1986), Bénézeth et al. (1997), and Uchida and Okuwaki (1998) is quite satisfactory. Second, relatively few experimental measurements were available to Baes and Mesmer (1986) on which to base their recommended values. Third, having carried out their experiments at an elevated temperature, Bénézeth et al. (1997) may have avoided problems with slow reaction kinetics. However, an extrapolation of

125 °C was required in their study, which increases the level of uncertainty. Obviously, additional investigation is required to resolve these discrepancies. Because the HKF-equation parameters of Bénézeth et al. (1997) are based on carefully performed experiments and allow estimation of Ga hydrolysis under hydrothermal conditions, we also employ their values of the hydrolysis constants of $Ga(OH)_2^+$, $Ga(OH)_3^0$, and $Ga(OH)_4^-$.

An alternate set of HKF-equation parameters have been published by Shock et al. (1997) based on the recommended hydrolysis constants of Baes and Mesmer (1986) and correlation algorithms developed by the former authors. Estimates of hydrolysis constants at saturated water vapor pressure (SWVP) obtained from the parameters of Shock et al. (1997) are compared with the analogous values of Bénézeth et al. (1997) in Fig. 2. In general, these two sets of estimates are within 2 log units of one another and in many cases are much closer, with the estimates of Bénézeth et al. (1997) being typically lower than those of Shock et al. (1997). In a recent experimental study, Wood et al. (2002) demonstrated that hydrolysis constants for Nd^{3+} at elevated temperatures (Haas et al., 1995), which were estimated using correlation algorithms of the type used by Shock et al. (1997), are probably higher than the true value. This also may be the case with Ga^{3+} and the other trivalent ions of interest in this paper.

The predicted distribution of hydrolyzed gallium species as a function of pH and temperature at SWVP is shown in Fig. 3. At 25 °C, $Ga(OH)_2^+$ and $Ga(OH)_3^0$ are not predominant at any pH, Ga^{3+} is predominant at pH values of less than 3, $Ga(OH)_4^-$ is predominant at pH >4, and $Ga(OH)^{2+}$ has a narrow field of predominance between pH 3 and 4. With increasing temperature, the predominance fields of Ga^{3+} and $Ga(OH)^{2+}$ shrink, while those of $Ga(OH)_2^+$ and $Ga(OH)_3^0$ increase. At all temperatures, $Ga(OH)_4^-$ has a substantial field of predominance but this field shifts slightly to higher pH with increasing temperature, such that by 300 °C, $Ga(OH)_4^-$ is only predominant at pH values greater

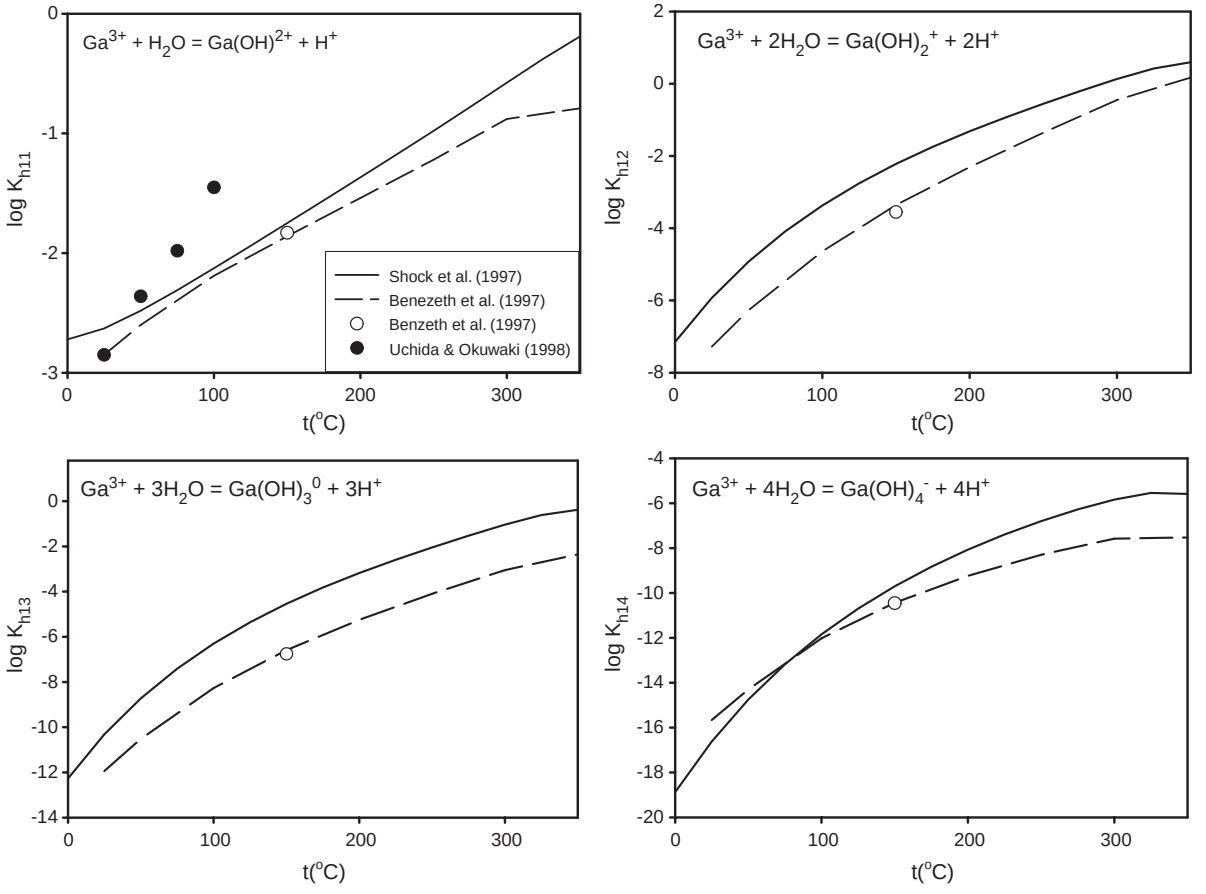

Fig. 2. Comparison of published hydrolysis constants for Ga^{3+} at infinite dilution, SWVP and elevated temperatures. The open and closed circles represent the experimental measurements of Bénézeth et al. (1997) and Uchida and Okuwaki (1998), respectively. The solid and dashed curves represent the values calculated from the HFK parameters reported by Shock et al. (1997) and Bénézeth et al. (1997), respectively.

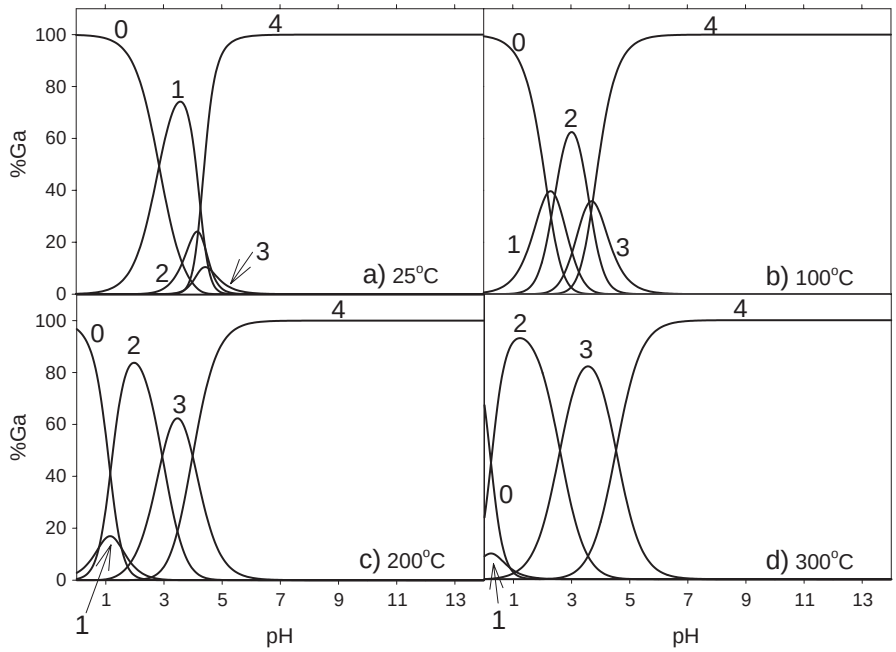

Fig. 3. Distribution of mononuclear Ga–hydroxide species as a function of temperature and pH at SWVP and infinite dilution. The species shown are: 0—Ga^{3+}; 1—$GaOH^{2+}$; 2—$Ga(OH)_2^+$; 3—$Ga(OH)_3^0$; and 4—$Ga(OH)_4^-$.

than 5. It is obvious from Fig. 3 that unhydrolyzed Ga^{3+} will play no significant role in the hydrothermal mass transfer of gallium.

4.3.2. Fluoride complexes

Gallium(III) forms comparatively strong complexes with fluoride. The stability constants of GaF^{2+} have been determined in several studies (Table 4; Fig. 4), and, with the exception of the data by Wilson and Taube (1952) and Mikhailyuk and Gordienko (1974), there is reasonable agreement when account is taken of the different ionic strengths. Regression of the available data leads to a stability constant at infinite dilution of log $\beta_1 = 5.1$, which we provisionally accept as a best estimate for this value at 25 °C. However, there are relatively few data, and the regressed value differs from the value at infinite dilution reported by Jablonski and Jablonski (1978) by almost 0.5 log units. Thus, there is considerable uncertainty attached to this value at present. There are far fewer measurements of the stability constants of GaF_2^+, GaF_3^0, and GaF_4^- (Kleiner and Gridchina, 1960; Yuchi et al., 1987). Thus, we refrain from recommending any values for these constants.

4.3.3. Chloride complexes

As mentioned above, Woodward and Nord (1956) report Raman spectroscopic evidence for the existence of the tetrahedral $GaCl_4^-$ ion in aqueous solutions of 6.3 M HCl. Relatively few measurements of the stability constants of Ga–chloride complexes have been carried out (Table 4), but the available data suggest that these complexes are quite weak. This behavior is similar to that of Al(III), for which chloride complexes do not

Table 4
Summary of stability constants of Ga^{3+}–fluoride and chloride complexes from the literature

Medium	Temperature (°C)	log β_n				
		GaF^{2+}	GaF_2^+	GaF_3^0	GaF_4^-	Source
0.5 M $NaClO_4$	25	5.01	–	–	–	52WT
0.004–0.04 M	20	4.54	8.34	11.1	12.6	60KG
0.004 M	20	4.51	–	–	–	60K
1 M $NaClO_4$	25	4.38	–	–	–	71W
1 M $NaClO_4$	25	3.3	–	–	–	74MG
0?	25	5.58	–	–	–	78JJ
0.1 M KNO_3	25	4.49	7.99	–	–	87Y
		$GaCl^{2+}$	$GaCl_2^+$	$GaCl_3^0$	$GaCl_4^-$	
0		−0.6	−2.30	−4.50	−5.80	54K
0.691 $HClO_4$	20	0.01	–	–	–	67MA
4 M $NaClO_4$		−0.24	−0.15	–	–	77SH

Sources: fluoride; 52WT—Wilson and Taube (1952); 60KG—Kleiner and Gridchina (1960); 60K—Kleiner (1960); 71W—Walker et al. (1971); 74MG—Mikhailyuk and Gordienko (1974); 78JJ—Jablonski and Jablonski (1978); 87Y—Yuchi et al. (1987); chloride; 54K—Kraus et al. (1954); 67MA—Morris and Andrews (1967); 77SH—Sekine and Hasegawa (1977).

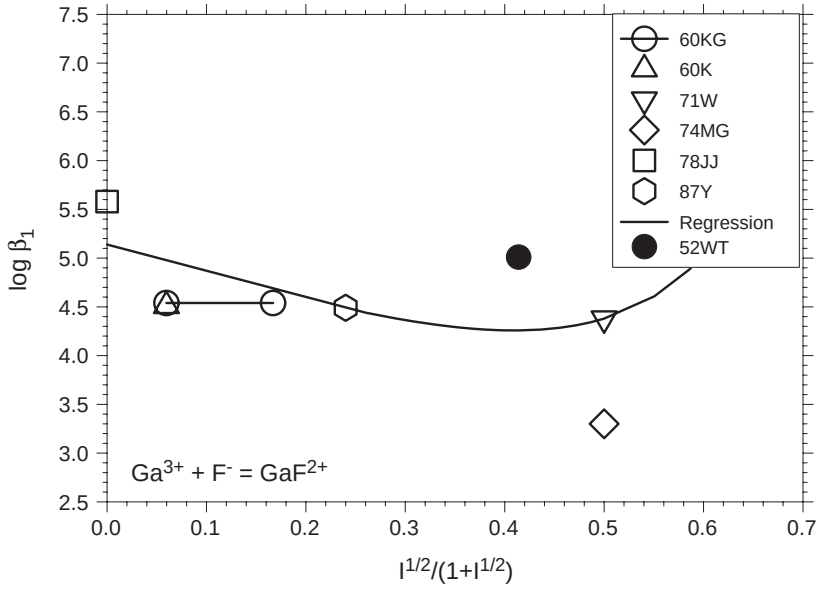

Fig. 4. Literature values of the stability constant for the species GaF^{2+} vs. $I^{½}/(1+I^{½})$, where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 4.

appear to be important in natural waters (Wesolowski, 1992; Palmer and Wesolowski, 1992).

The thermodynamic properties (heats of solution, heats of dilution, heat capacities, molar volumes) of aqueous $GaCl_3$ solutions were determined by van Gaans et al. (1990) and van Gaans and van Miltenburg (1991). These data were modeled using the Pitzer (ion interaction) activity coefficient model. In this approach, the thermodynamic effect of weak interactions between Ga^{3+} and Cl^- ions is incorporated into the various Pitzer parameters, and there is no need to account explicitly for Ga-chloride complexation using stability constants. That such an approach was successful in describing the experimental data is further confirmation that Ga–chloride complexes are comparatively weak.

4.3.4. Sulfate and phosphate complexes

Relatively little information on the composition and stability of complexes of Ga(III) with sulfate is available (Table 5). Nanda and Aditya (1962), Izatt et al. (1969), Kalidas et al. (1971) and Schischkova (1974) determined the stability constant of $GaSO_4^+$, and these appear to be in reasonable agreement given the differences in ionic strength and temperature. Only Izatt et al. (1969) have measured a stability constant for $Ga(SO_4)_2^-$. The stability constants that Izatt et al. (1969) obtained for other metal–sulfate complexes agree reasonably well with the most reliable stability constants obtained in other studies, so we adopt their values in this study. Izatt et al. (1969) also provide enthalpies of complexation which are a prerequisite to the estimation of stability constants at elevated temperatures. The data in Table 5 suggest relatively weak complexing of sulfate with Ga(III), compared to hydroxide and fluoride, so that Ga–sulfate complexes probably play a limited role in Ga transport.

Data for Ga(III)–phosphate complexes are even sparser (Table 6). Filatova and Galochkina (1974) and Mikhailyuk and Gordienko (1975) determined stability constants for $GaHPO_4^+$ and $Ga_2(HPO_4)^{4+}$, respectively. These complexes seem to be quite stable, but not much more can be said with the limited data available.

4.3.5. Mixed-ligand complexes

Tóth et al. (1985) interpreted spectrophotometric and potentiometric measurements in terms of the formation of a mixed-ligand complex of gallium with hydroxide

Table 5
Summary of stability constants of Ga^{3+}–sulfate complexes from the literature

Medium	Temperature (°C)	log β_n		
		$GaSO_4^+$	$Ga(SO_4)_2^-$	Source
0	30	2.99	–	62NA
0	25	2.77	5.06	69I
0?	25	2.59	–	71K
1 M $NaClO_4$	20	1.10	–	74S

Sources: 62NA—Nanda and Aditya (1962); 69I—Izatt et al. (1969); 71K—Kalidas et al. (1971); 74S—Schischkova (1974).

Table 6
Summary of stability constants of Ga^{3+}, In^{3+} and Sc^{3+}–phosphate complexes from the literature

Metal (Me)	Medium	Temperature (°C)	log β_n				
			$Me(HPO_4)^+$	$Me(HPO_4)_2^-$	$Me(H_2PO_4)^{2+}$	$Me_2(HPO_4)^{4+}$	Source
Ga	0.2 M	25?	–	–	–	7.73	74FG
	1 M $NaClO_4$	25	7.26	–	1.48	–	75MG
In	0.2 M	25?	7.40	13.71	–	–	80F
	0.2 M	25?	–	–	–	8.90	74FG
	0.9 M	20	–	–	1.43	–	74FK
Sc	0	25	–	–	4.72	–	70L
	0.6 M $NaClO_4$	25	–	–	3.76	–	70L
	0.2 M	25?	–	–	–	13.3	74FG

Sources: 74FG—Filatova and Galochkina (1974); 74FK—Filatova and Kurdyumova (1974); 75MG—Mikhailyuk and Gordienko (1975); 80F—Filatova (1980); 70L—Laskorin et al. (1970).

and sulfide, i.e., $Ga(OH)_2S^-$. However, these same authors sought, but did not find, evidence for the formation of mixed hydroxy–fluoride and hydroxy–chloride complexes. Tóth et al. (1985) acknowledged that they could not distinguish between the alternative stoichiometries $Ga(OH)_2S^-$ and $Ga(OH)_3(HS)^-$ for the mixed hydroxy–sulfide complex. They note that this complex would be most important at a pH near 9 at 25 °C and would become less important with increasing pH. In our opinion, although such a mixed complex may play a role as an intermediate step in the incorporation of Ga into sulfide minerals, it is unlikely to be responsible for significant mass transfer in natural aqueous solutions.

4.4. Germanium

4.4.1. Germanic acid and its dissociation products

Similar to silicon, the most important forms of germanium in aqueous solution are germanic acid ($H_4GeO_4^0$) and its dissociation products (e.g., $H_3GeO_4^-$ and $H_2GeO_4^{2-}$). Polynuclear Ge(IV) species have been investigated by Carpéni (1948), Lourijsen-Teyssèdre (1955), Antikainen (1960), Ingri (1963), Ingri and Schorsch (1963), Haas et al. (1964a,b,c) and De la Cuadra (1990). The studies of germanic acid dissociation and polynuclear germanium species prior to 1976 were reviewed by Baes and Mesmer (1986) and the latter contains additional references on polynuclear species. It is unlikely that polynuclear species play a significant role in the transport of Ge in natural solutions because dissolved Ge concentrations would likely be too low to stabilize such species. However, as was the case with Ga, the polynuclear species are relevant in that their presence complicates the interpretation of experiments designed to measure the dissociation constants of germanic acid.

Measured first and second dissociation constants of germanic acid are given in Table 7 and Fig. 5. Several of the earlier studies are affected by the presence of polynuclear species and therefore there is considerable spread among these values. If the results of Roth and Schwartz (1926), Schwarz and Huf (1931) and Gayer and Zajicek (1964) are excluded, then all of the other measurements of the first dissociation constant lie within a comparatively narrow range of $10^{-9.4}$ to $10^{-8.4}$, and are reasonably independent of ionic strength (Fig. 5a). The recent measurement of the first dissociation constant by Pokrovski and Schott (1998) are in good agreement with the majority of the earlier measurements and these authors also obtained data up to 200 °C. Kosova and Dem'yanets (1988) report dissociation constants up to 300 °C, but their data disagree by more than a log unit with those of Pokrovski and Schott (1998) at 200 °C. The data of the latter parallel the trend with respect to temperature established for silicic acid by Busey and Mesmer (1977). Therefore, we recommend use of the data of Pokrovski and Schott (1998) for the first dissociation constant of germanic acid. There are far fewer measurements of the second dissociation constant but all fall in the range $10^{-12.7}$ to $10^{-11.7}$ (Fig. 5b). These values suggest that the species $H_2GeO_4^{2-}$ will be predominant only at pH values greater than 11.7 (at 25 °C) meaning that it will probably not play a significant role in germanium transport in most natural environments.

Nazarenko et al. (1962), Andrianov and Nazarenko (1966), Nazarenko and Flyantikova (1968), and Alekseeva and Nemzer (1971) report the existence of cationic species of Ge(IV), e.g., Ge^{4+}, $Ge(OH)^{3+}$, $Ge(OH)_2^{2+}$, and $Ge(OH)_3^+$. Baes and Mesmer (1986) questioned the evidence presented in these studies and believed that no accurate estimates of the stabilities of cationic Ge(IV) species existed. Even if such species do

Table 7
Summary of dissociation constants of H_4GeO_4 from the literature

Medium	Temperature (°C)	log K_{diss}*		
		$H_4GeO_4^0$	$H_3GeO_4^-$	Source
0	18	−6.92	–	26RS
0?	20	−8.68	−12.72	29P
0?	20	−8.49	–	29P
0?	20	−7.30	–	31SH
0	25	−8.8	–	32GM
2 M KCl	12	−9.1	−12.7	48C
0.5 m Na_2SO_4	25?	−9.08	–	55LT
0	10	−9.045	–	57A
0	15	−8.980	–	57A
0	20	−8.920	–	57A
0	25	−8.730	–	57A
0	30	−8.615	–	57A
0	35	−8.450	–	57A
0	40	−8.175	–	57A
0	45	−7.900	–	57A
sat'd Na_2SO_4	32	–	−12.31	58KT
3 M NaCl	25	–	−12.43	63IS
0.5 m NaCl	25	−9.02	–	63I
0.5 m $NaClO_4$	25	−9.016	–	64H
1.0 m $NaClO_4$	25	−9.016	−11.74	64H
0	25	−11.56	–	64GZ
0.1 M KNO_3	20	−9.27	–	79MB
0	25	−9.31	−12.59	86BM
0.1 M KCl	25	−9.26	–	86H
0	25	−9.31	–	88KD
0	50	−9.34	–	88KD
0	100	−9.49	–	88KD
0	150	−9.70	–	88KD
0	200	−9.98	–	88KD
0	250	−10.32	–	88KD
0	300	−10.76	–	88KD
0	25	−9.32 ± 0.05	–	98PS
0	50	−8.92	–	98PS
0	75	−8.70	–	98PS
0	100	−8.55	–	98PS
0	125	−8.48	–	98PS
0	150	−8.41	–	98PS
0	175	−8.35	–	98PS
0	200	−8.37	–	98PS

Sources: 26RS—Roth and Schwartz (1926); 29P—Pugh (1929); 31SH—Schwarz and Huf (1931); 32GM—Gulezian and Müller (1932), but K_1 from this source is given by Baes and Mesmer (1986) as −9.3; 48C—Carpéni (1948); 55LT—Lourijsen-Teyssèdre (1955); 57A—Antikainen (1957); 58KT—Krüger and Thilo (1958); 63IS—Ingri and Schorsch (1963); 63I—Ingri (1963); 64GZ—Gayer and Zajicek (1964); 64H—Haas et al. (1964a); 79MB—Mikešová and Bartušek (1979); 86BM—recommended values from critical review by Baes and Mesmer (1986); 86H—Häkkinen et al. (1986); 88KD—Kosova and Dem'yanets (1988); 98PS—Pokrovski and Schott (1998).
*Reactions: $H_4GeO_4^0$: $H_4GeO_4^0 \leftrightarrow H_3GeO_4^- + H^+$
$H_3GeO_4^-$: $H_3GeO_4^- \leftrightarrow H_2GeO_4^{2-} + H^+$.

exist, it would be only in very acidic solutions and hence they are of no relevance to Ge transport in most natural solutions.

4.4.2. Fluoride complexes

Fluoride is probably the only ligand considered in this paper that is capable of displacing oxygen from the coordination sphere of Ge(IV) under geologically reasonable conditions, and even in this case, replacement is rarely complete. Several experimental studies of fluoride complexes of germanium(IV) have been conducted at room temperature. Using solvent extraction, solubility, and potentiometric methods, Benoit and Place (1963) found evidence for species of the general form $GeF_4(OH)_i$ and $GeF_5(OH)_i$, but they did not determine the value of i. In a series of papers, Ryss and Kulish (1964a,b, 1965) investigated the hydrolysis of the hexafluorogermanate ion GeF_6^{2-} and concluded that the following species are formed: $GeF_5(H_2O)^-$ and $Ge(OH)F_4(H_2O)^-$. Parpiev and Maslennikov (1968) reported a formation constant for GeF_6^{2-}. From potentiometric measurements with a fluoride-selective electrode, Ciavatta et al. (1990) deduced the existence of the species GeF_4^0, $Ge(OH)F_4^-$, GeF_6^{2-}, $HGeF_6^-$, and possibly $Ge(OH)F_2^+$. Owing to the lack of agreement regarding the stoichiometries of the predominant Ge–fluoride and –hydroxyfluoride species, we refrain from recommending stability constants at the present time. However, this issue requires some experimental attention as such species could potentially play a role in Ge mass transfer in fluoride-rich environments, such as those in which greisenization occurs.

4.4.3. Chloride complexes

It is expected that, in accordance with Pearson's (1963) rule, the soft chloride ion would displace hard O^{2-} from the coordination sphere of hard Ge(IV) only with great difficulty. Indeed, a solvent extraction study by Sohrin (1991) indicates that, at 25 °C, chloride complexes do not become important until the concentration of HCl exceeds 4 mol L^{-1}. This agrees with the solvent extraction results of Benoit and Clerc (1961) who found that germanic acid was the main Ge species up to 5.6 m HCl. We therefore do not expect Ge–chloride complexes to play any significant role in the hydrothermal mass transfer of Ge. There are no data available for sulfate or phosphate complexes of Ge, but it seems unlikely that these ligands would play an important role in hydrothermal transport of Ge, based on the analogy with Si.

4.5. Indium

The In^{3+} ion forms more stable chloride complexes than its smaller congeners in the periodic table (Al^{3+} and Ga^{3+}), but its mononuclear hydroxide complexes have intermediate stability compared to the latter ions

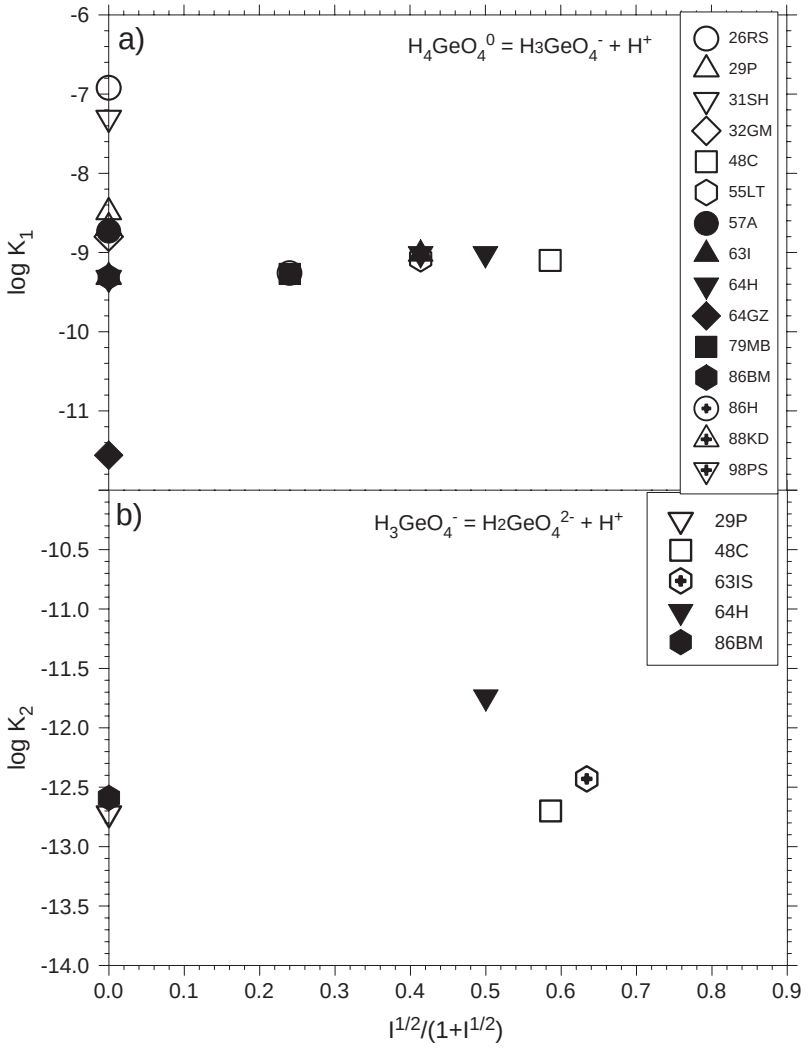

Fig. 5. Literature values of the (a) first and (b) second dissociation constants of germanic acid vs. $I^{1/2}/(1+I^{1/2})$, where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 7.

(Baes and Mesmer, 1986). Stability constants for a variety of inorganic and organic complexes of In^{3+} have been reviewed critically by Tuck (1983). The structure of the hydrated In^{3+} ion has been studied using X-ray diffraction methods by Maeda and Ohtaki (1977) and Caminiti and Paschina (1981), and using EXAFS by Lindqvist-Reis et al. (1998). These studies have shown that the hydrated In^{3+} ion is coordinated by six water molecules with an In–OH_2 bond distance of 2.15 ± 0.03 Å. Additional evidence for the octahedral coordination of In^{3+} by water is reviewed by Tuck (1983) who concludes that, in the absence of hydrolysis, complex formation of In^{3+} with a ligand (L) should be considered to take place according to:

$$In(H_2O)_6^{3+} + nL^{z-} \leftrightarrow In(H_2O)_{6-n}L_n^{3-nz} + nH_2O. \quad (6)$$

EXAFS measurements on In^{3+} solutions up to 250 °C by Seward et al. (2000) indicate that, in the absence of ligands other than water, the hydrated In^{3+} ion is coordinated by six water molecules in an octahedral arrangement with a constant In^{3+}–OH_2 distance of 2.14 ± 0.01 Å. Thus, the maximum coordination number of In^{3+} in aqueous solution does not seem to change with increasing temperature up to at least 250 °C.

4.5.1. Hydroxide

Mononuclear hydroxide complexes of the types $InOH^{2+}$, $In(OH)_2^+$, $In(OH)_3^0$ and $In(OH)_4^-$ have been discussed in numerous studies and published estimates of the hydrolysis constants for these species are given in Table 8. In addition, the following polynuclear species have been proposed: $In_2(OH)_2^{4+}$ (Biedermann et al.,

Table 8
Summary of In^{3+} hydrolysis constants from the literature

Medium	Temperature (°C)	log K_{hpq}				
		$InOH^{2+}$	$In(OH)_2^+$	$In(OH)_3^0$	$In(OH)_4^-$	Source
0.006 M $In_2(SO_4)_3$	25	−3.7	–	–	–	36HD
0	23	−3.87	–	–	–	52HH
3 M $NaClO_4$	25	−4.4	−8.8	–	–	56RR
3 M $NaClO_4$	25	−4.25	−8.53	–	–	56B
0	25	–	–	< −12.4	−22.07	59BT
1 M?	20	−2.11	−4.56	−7.24	–	65H
3 M $NaClO_4$	25	−4.7	–	–	–	67SW
3 M $NaClO_4$	25	−4.63	−9.01	–	–	69ALa
0	25	−3.54	−7.82	−12.98	–	69B
0.1 M $NaClO_4$	25	−3.48	−7.67	−12.75	–	69B
0.3 M $NaClO_4$	25	−3.40	−7.41	−12.37	–	69B
0.5 M $NaClO_4$	25	−3.33	−7.25	−12.10	–	69B
1 M $NaClO_4$	25	−3.11	−6.65	−11.13	–	69B
≤0.0005 M	25	−5.0	–	–	–	70H
3 M LiCl	25	−4.22	−7.14	–	–	74K
3 M $LiClO_4$	25	−4.24	−7.12	–	–	75Ka
3 M $LiClO_4$	25	−4.26	−7.10	–	–	75Kb
2 M $NaClO_4$	25	−2.39	−4.76	–	–	77L
1 M $LiClO_4$	25	−4.07	−6.88	–	–	80YR
0	25	−3.66	−6.06	–	–	81Y
0.1 M $LiClO_4$	25	−4.00	−6.79	–	–	81Y
0.3 M $LiClO_4$	25	−4.04	−6.81	–	–	81Y
1 M $LiClO_4$	25	−4.15	−6.98	–	–	81Y
0	25	−3.66	−6.06	–	–	81YR
0.1 M $LiClO_4$	25	−4.00	−6.79	–	–	81YR
0.3 M $LiClO_4$	25	−4.04	−6.81	–	–	81YR
1 M $LiClO_4$	25	−4.15	−6.98	–	–	81YR
0.1 M KNO_3	25	−4.31	−9.35	–	–	82B
0.5 M KNO_3	25	–	–	−11.0	–	84T
0	25	−4.00	−7.82	−12.4	−22.07	86BM
0.1 M $NaNO_3$	25	−3.78	–	–	–	91D

Sources: 36HD—Hattox and DeVries (1936); 52HH—Hepler and Hugus (1952) from data of Moeller (1941); 56RR—Rossotti and Rossotti (1956); 56B—calculated by least squares from data of Biedermann (1956a) by Baes and Mesmer (1986); 59BT—calculated by Baes and Mesmer (1986) from solubility of $In(OH)_3$ using data from Bereslavtseva and Toropova (1959); 65H—Hamid et al. (1965); 67SW—recalculated from the data of Rossotti and Rossotti (1956) by Schweitzer and Winkley (1967); 69ALa—Aziz and Lyle (1969a); 69B—Biryuk et al. (1969); 70H—Hemmes et al. (1970); 74K—Kul'ba et al. (1974); 75Ka—Kul'ba et al. (1975a); 75Kb—Kul'ba et al. (1975b); 77L—Lasztity (1977); 80YR—Yakovlev and Ravlenko (1980); 81Y—Yakovlev et al. (1981); 81YR—Yakovlev and Ravlenko (1981); 82B—Brown et al. (1982); 84T—Tóth et al. (1984); 86BM—recommended values from critical review by Baes and Mesmer (1986); 91D—Duma et al. (1991).

1961; Gordienko, 1974; Biedermann and Ferri, 1982), $In((OH)_2In)_n^{3+n}$ (Biedermann, 1956), $In_4(OH)_4^{8+}$ or $In_5(OH)_5^{10+}$ (Brown et al., 1982), $In_2(OH)_3^{3+}$ and $In_2(OH)_4^{2+}$ (Gordienko, 1974), and $In_4(OH)_6^{6+}$ (Biedermann and Ferri, 1982). Jander and Pluskal (1957) inferred the presence of polynuclear species from diffusion measurements but did not determine the stoichiometry. Baes and Mesmer (1986) concluded that the data of Biedermann (1956) could just as easily be explained by a single polynuclear complex, e.g., $In_3(OH)_4^{5+}$, instead of the series of species of general formula $In((OH)_2In)_n^{3+n}$ originally proposed by Biedermann (1956). Baes and Mesmer (1986) acknowledged the probability that a series of polynuclear species does exist, but point out that the data were insufficient to determine the identity of these species. As is the case for Ga and Ge, polynuclear species are probably not important in the aqueous transport of indium in geological environments, but their presence in many experimental solutions has a bearing on the ability to determine thermodynamic data for the mononuclear species. At least part of the reason for observed discrepancies in the hydrolysis constants for mononuclear species may be incorrect assumptions regarding the polynuclear species present.

The published estimates of hydrolysis constants for the species $InOH^{2+}$, $In(OH)_2^+$, $In(OH)_3^0$ are shown in Fig. 6. The data for K_{h11} reported by Hamid et al.

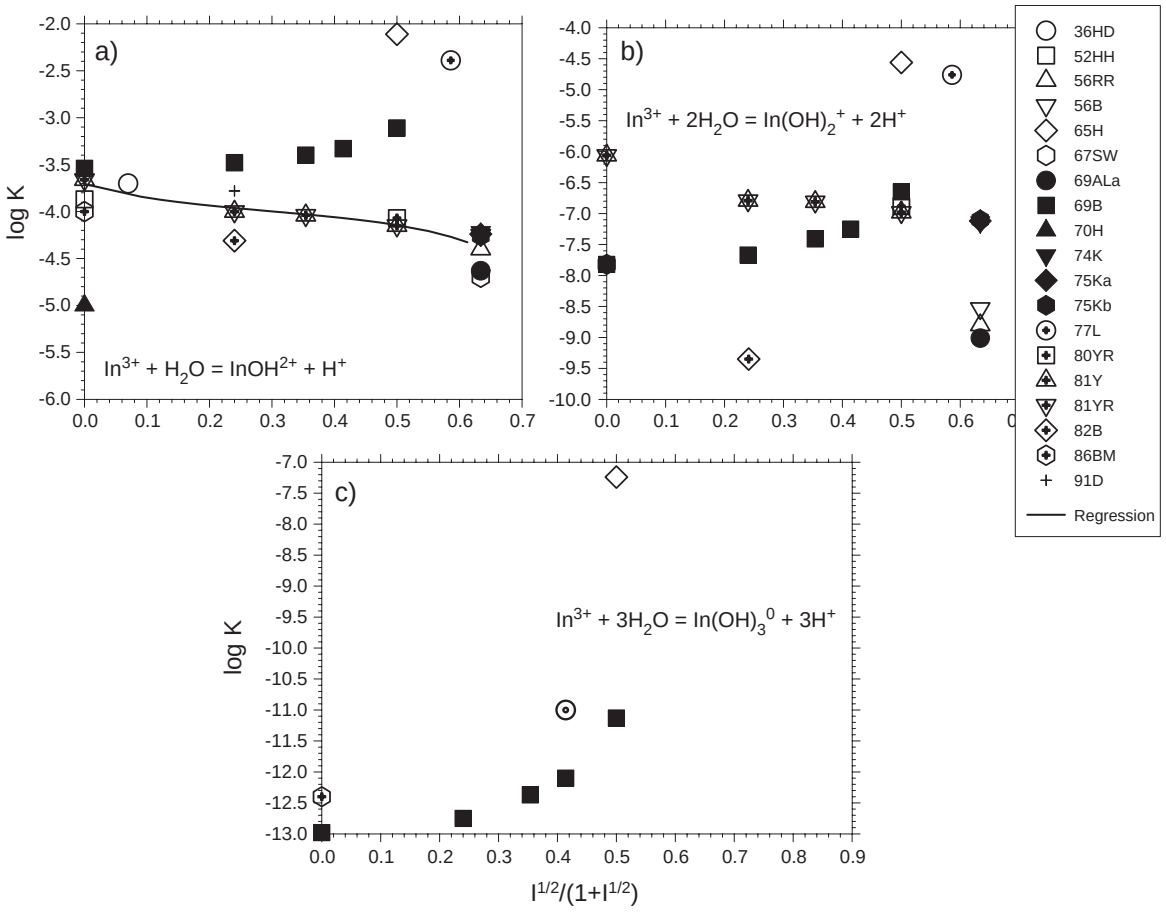

Fig. 6. Literature values of the hydrolysis constants for (a) $InOH^{2+}$; (b) $In(OH)_2^+$; and (c) $In(OH)_3^0$ vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 8.

(1965), Biryuk et al. (1969), Hemmes et al. (1970) and Lasztity (1977) are in severe disagreement with the remaining data (all of which are within approximately 0.5 log units of each other at a given ionic strength) and must be considered to be in error. In fact, the data of Biryuk et al. (1969) exhibit an ionic strength dependence contrary to that expected. Of the remaining data for K_{h11}, those determined by Hattox and de Vries (1936) and Moeller (1941) are compromised by sulfate complexation and chloride complexation, respectively. However, Hepler and Hugus (1952) made a correction to the data of Moeller (1941) to account for chloride complexation. At an ionic strength of 3 M, there is excellent agreement among the data of Biedermann (1956), Rossotti and Rossotti (1956), and Kul'ba et al. (1974, 1975a,b), and so these data can be considered to be the most reliable. Unfortunately, extrapolation from such a high ionic strength to infinite dilution is prone to considerable uncertainty. Baes and Mesmer (1986) recommend a value of K_{h11} at infinite dilution that is based on an extrapolation of the data of Biedermann (1956), and their value is in excellent agreement with the value calculated by Hepler and Hugus (1952) from Moeller's (1941) data, and is in reasonable agreement with data of Yakovlev et al. (1981) and Yakovlev and Ravlenko (1981). Given the above, we tentatively accept the estimate of Baes and Mesmer (1986) for K_{h11} at infinite dilution.

The situation worsens considerably for higher, mononuclear hydrolysis products of In^{3+}. In general, as the number of hydroxide ions bound to In^{3+} increases, the number of estimates of the hydrolysis constants decreases, as does the degree of agreement among the various studies. We tentatively accept the estimates provided by Baes and Mesmer (1986) for K_{h12}, K_{h13}, and K_{h14}. However, it is clear that additional, reliable, experimental measurements are required.

We are unaware of any experimental measurements of In^{3+} hydrolysis at temperatures above 25 °C, although enthalpies of hydrolysis were measured in 3

M $NaClO_4$ for the first two hydroxide species by Schlyter (1961), resulting in $\Delta H_{h11} = 20.3 \pm 3.8$ kJ mol^{-1} and $\Delta H_{h12} = 59 \pm 38$ kJ mol^{-1}. However, extrapolation of these enthalpies to infinite dilution is problematic. Shock et al. (1997) provide parameters for the HKF equation, based on the estimates of Baes and Mesmer (1986), that permit estimation of the hydrolysis constants of In^{3+} at elevated temperatures and pressures. Owing to the scarcity of data at 25 °C and 1 bar and the complete lack of data at higher temperatures and pressures, these estimates must be considered provisional. However, they may be used to draw some tentative conclusions regarding the distribution of In(III)-hydroxide species as a function of temperature and pH. From Fig. 7, it is evident that the unhydrolyzed In^{3+} ion is predicted to be predominant only at pH values less than ~4 at 25 °C, and at 300 °C the unhydrolyzed ion is predominant only at a pH <1. Thus, in the absence of other ligands, hydrolyzed forms dominate In(III) speciation under geologically reasonable conditions. It is also predicted that the first mononuclear hydrolysis product, $InOH^{2+}$, is relatively unimportant, never accounting for more than 30% of total In at 25 °C, and this percentage decreases with increasing temperature. Even the second hydrolysis product, $In(OH)_2^+$, has a relatively narrow field of predominance. In most geological environments, $In(OH)_3^0$ and $In(OH)_4^-$ are predicted to be the most important species (in the absence of other ligands), and $In(OH)_4^-$ predominates at increasingly lower pH values as temperature increases. However, we again caution that these predictions require experimental verification.

4.5.2. Fluoride complexes

Stability constants have been reported for complexes of the form InF_n^{3-n}, for $n = 1$–4 (see Table 9 and Fig. 8). With the following exceptions, there is good to excellent agreement among the various studies. The data from Schufle and Eiland (1954) are clearly in disagreement with the bulk of the other data, and the data of Yuchi et al. (1987) also appear to be too low compared to the other data. Tuck (1983) attributes the discrepancy in the data of the former authors to the high pH employed in their experiments, which probably led to significant, unaccounted-for hydrolysis. The data reported by Vasil'ev and Kozlovskii (1974) represent extrapolations of the experimental results of Ryhl (1969). The agreement among the studies is best for β_1 and degrades somewhat as the number of fluoride ions in the complex increases. For β_1 and β_2, our extrapolation using Eq. (5) falls within 0.3 log units of the extrapolated value of Vasil'ev and Kozlovskii (1974), and so the extrapolated values are probably reasonably reliable. For β_3, the difference in our extrapolated value and that of Vasil'ev and Kozlovskii (1974) is more than 0.8 log units. We therefore attach a

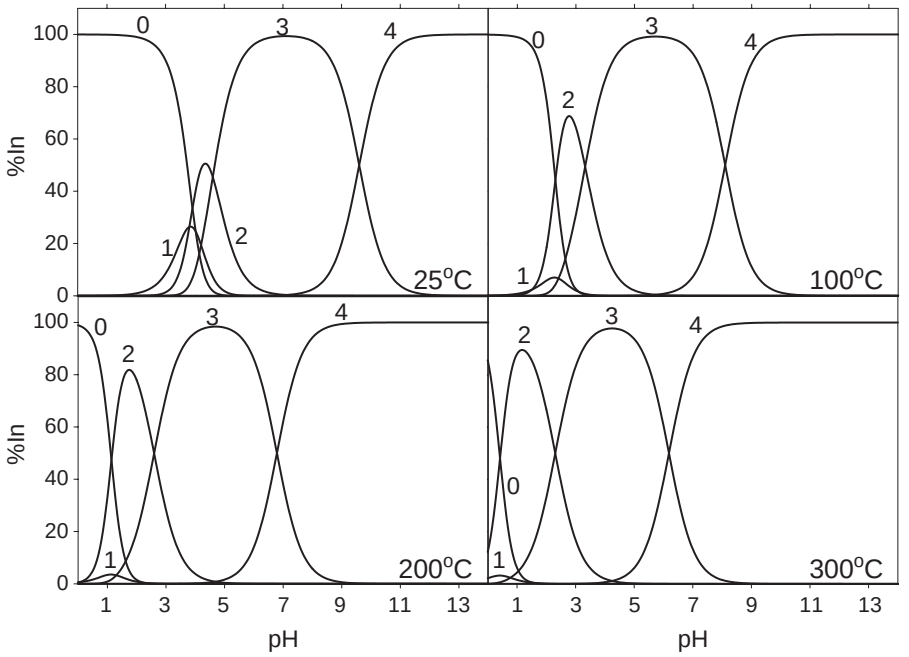

Fig. 7. Distribution of mononuclear In–hydroxide species as a function of temperature and pH at SWVP and infinite dilution. The species shown are: 0—In^{3+}; 1—$InOH^{2+}$; 2—$In(OH)_2^+$; 3—$In(OH)_3^0$; and 4—$In(OH)_4^-$.

Table 9
Summary of stability constants of In^{3+}–fluoride complexes from the literature

Medium	Temperature (°C)	$\log\beta_n$				
		InF^{2+}	InF_2^+	InF_3^0	InF_4^-	Source
0.5 M	25	3.78	6.41	–	–	54CI
1 M $NaClO_4$	25	3.0	5.8	8.6	–	54SE
1 M $NaClO_4$	25	3.67	6.26	8.61	–	68AL
1 M $NaClO_4$	25	3.69	6.52	8.63	9.90	69R
1 M $NaClO_4$	25	3.72	–	–	–	71W
0.5 M $NaClO_4$	25	3.72	6.39	9.95	–	73B
0	25	4.66	8.12	10.27	11.54	74VK
0.5 M	25	3.75	6.61	8.60	9.87	74VK
2 M	25	3.74	6.63	9.04	10.31	74VK
2 M $NaClO_4$	20	3.7	6.26	8.62	9.71	83T
0.1 M KNO_3	25	3.64	6.54	–	–	87Y

Sources: 54CI—recalculated from the measurements of Hepler et al. (1954) by Carleson and Irving (1954); 54SE—Schufle and Eiland (1954); 68AL—Aziz and Lyle (1968); 69R—Ryhl (1969); 71W—Walker et al. (1971); 73B—Bottazzini et al. (1973); 74VK—calculated from the data of Ryhl (1969) by Vasil'ev and Kozlovskii (1974); 83T—recalculated from the measurements of Sundén (1954a) by Tuck (1983); 87Y—Yuchi et al. (1987).

much greater uncertainty to β_3, than to β_1 and β_2. We tentatively accept the value of β_4 at infinite dilution determined by Vasil'ev and Kozlovskii (1974), but this value is uncertain by more than a log unit.

Stability constants for In–fluoride complexes at elevated temperatures and pressures have not been determined to our knowledge. However, several authors have reported enthalpies of complexation (Table 10). The spread in the values obtained in the various studies is relatively large (for example, the enthalpy for the first complexation reaction at 1 M ionic strength ranges over more than 3 kJ mol^{-1} among three studies). Although the enthalpies for the first and second complexation reactions measured by Ryhl (1969) and Vasil'ev and Kozlovskii (1974) are within experimental error of one another, their enthalpies for the third complexation reaction vary by a factor of 2. These discrepancies, and the uncertain extrapolation required to obtain enthalpies at infinite dilution, hinder accurate prediction of stability constants of In–fluoride complexes to elevated temperatures.

Parameters for the HKF equation, which permit estimation of the stability constant for InF^{2+}, have been compiled by Sverjensky et al. (1997) based on thermodynamic data reviewed by Turner et al. (1981) and correlation algorithms. The stability constant (log β_1) calculated from these parameters for 25 °C is 4.6, only 0.3 log units different from the value we adopted in this study (4.9). Furthermore, the former is similar to the value (log β_1=4.66) estimated by Vasil'ev and Kozlovskii (1974) based on the data of Ryhl (1969). Thus, the HKF parameters published by Sverjensky et al. (1997) may provide reasonable estimates for the stability constant of InF^{2+} as a function of temperature, but are essentially untested. No attempt was made by Sverjensky et al. (1997) to determine HKF parameters for the other In–fluoride complexes.

4.5.3. Chloride complexes

Table 11 and Fig. 9 summarize the data available on stability constants for In–chloride complexes. There is convincing evidence for the formation of the species $InCl^{2+}$, $InCl_2^+$, $InCl_3^0$, and $InCl_4^-$ at 25 °C, although the fourth complex appears to be relatively unstable. For example, Schufle et al. (1951) showed that $InCl_4^-$ is stable only at very high chloride concentrations (~8 M), and in the study of Kondziela and Biernat (1975), the measured value of β_4 is less than that of β_3. EXAFS data at 25 °C (Seward et al., 2000) yield evidence for $InCl_4^-$ in concentrated HCl solutions. Higher species (e.g., $InCl_5^{2-}$ and $InCl_6^{3-}$) were not detected in Raman studies of the In(III)–chloride system at chloride concentrations as high as 2 M (Hanson and Plane, 1969) and 10 M (Jarv et al., 1977), contradicting the earlier Raman study of Woodward and Taylor (1960). On the other hand, Ferri et al. (1994) inferred the presence of $InCl_4^-$, $InCl_5^{2-}$, and $InCl_6^{3-}$ in solutions containing up to 5 M chloride from a potentiometric investigation. They determined the following stability constants at 25 °C and 5 M ionic strength: log $\beta_4=3.59\pm0.03$; log $\beta_5=2.65\pm0.03$; and log $\beta_6=2.18\pm0.03$. If $InCl_5^{2-}$ and $InCl_6^{3-}$ exist, they probably play limited roles in the aqueous mass transfer of In, especially at elevated temperatures where the tendency is towards species of lesser charge as the dielectric constant of water decreases (Crerar et al., 1985).

Fig. 9a shows that, for β_1 for In(III)–chloride complexes, the agreement among the various studies is reasonably good (given the differences in ionic strengths), with the exception of the results of Schufle and Eiland (1954), Altynov and Ptitsyn (1962), and Mikhailova et al. (1969) which are clearly too low compared to the rest of the data, and the result of Cozzi and Vivarelli (1953, 1954) which is clearly too high. A regression fit of Eq. (5) to the more reliable data yields a value for β_1 at infinite dilution that is very close to the value recommended by Baes and Mesmer (1986). In the case of β_2, the agreement is considerably poorer (Fig. 9b), with the values of Cozzi and Vivarelli (1953, 1954), Schufle and Eiland (1954), and Altynov and Ptitsyn (1962) again being clearly anomalous. For

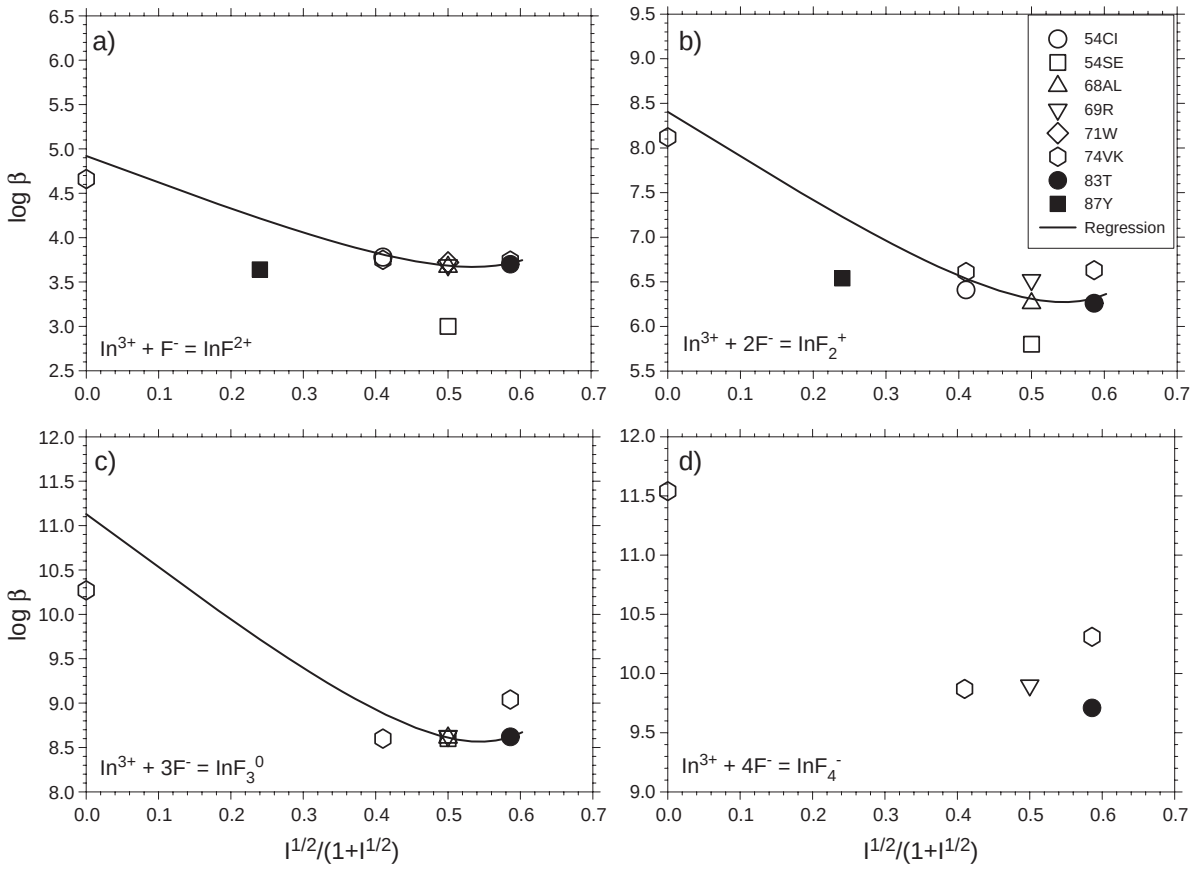

Fig. 8. Literature values of the stability constants for (a) InF^{2+}; (b) InF_2^+; (c) InF_3^0; and (d) InF_4^- vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 9.

β_2, the values of Zelyanskaya et al. (1958), Fridman et al. (1962) and Vavra and Rundenko (1964) also scatter far from the rest of the data. Measured values of β_3 seem to group together somewhat more tightly than those for β_2, but they still range over more than one log unit at a given ionic strength (Fig. 9c). The estimates of Baes and Mesmer (1986) of the values of all three stability constants (β_1, β_2, and β_3) at infinite dilution seem quite reasonable when compared to the reliable experimental data, and so we accept these estimates as the best currently available.

To our knowledge, there are no experimental measurements of the stability constants of In(III)–chloride complexes at elevated temperatures, although Ryhl (1969) determined enthalpies of the first three complexation reactions calorimetrically at 2.0 M ionic strength. The EXAFS measurements of Seward et al. (2000) on In(III) solutions at 25 °C in 0.1 mol HCl solutions demonstrated that octahedrally coordinated chloride complexes ($InCl_n(H_2O)_{6-n}^{3-n}$, where $0 \le n \le 4$) predominate. However, as temperature increases, the tetrahedrally coordinated species $InCl_4^-$ becomes increasingly

Table 10
Comparison of measured enthalpies of reaction from the literature for the reaction: $In^{3+} + nHF^0 \leftrightarrow InF_n^{3-n} + nH^+$

Medium	Temperature (°C)	ΔH (kJ mol^{-1})				
		InF^{2+}	InF^{2+}	InF_3^0	InF^{4-}	Source
0.5 M $NaClO_4$	25	10.3	–	–	–	54H
1 M $NaClO_4$	25	9.20 ± 0.17	7.7 ± 0.4	13.8 ± 1.3	–	69R
1 M $NaClO_4$	25	12.5 ± 0.6	–	–	–	71W
1 M $NaClO_4$	25	8.9 ± 0.2	8.3 ± 0.6	6.9 ± 1.0	10 ± 2	74VK

Sources: 54H—Hepler et al. (1954); 69R—Ryhl (1969); 71W—Walker et al. (1971); 74VK—Vasil'ev and Kozlovskii (1974). Values given are as quoted by Tuck (1983).

Table 11
Summary of stability constants of In^{3+}–chloride and –hydroxychloride complexes from the literature

Medium	Temperature (°C)	log β_n						
		$InCl^{2+}$	$InCl_2^+$	$InCl_3^0$	$InCl_4^-$	$InOHCl^+$	In_2OHCl^{4+}	Source
<0.04 M	25	2.35	–	–	–	–	–	55HH
2 M $NaClO_4$	25	4.3	6.1	–	–	–	–	53,54CV
0.691 M $HClO_4$	20	2.36	3.63	3.95	–	–	–	54CI
1 M $NaClO_4$	25	1.41	2.23	3.23	–	–	–	54SE
2 M $NaClO_4$	20	2.15	3.59	–	–	–	–	54Sb
1 M $NaClO_4$	25	2.19	3.54	–	–	–	–	54Sc,d
0	25	–	6.28	–	7.44	–	–	58Z
0.7 M $HClO_4$	20	2.36	3.57	3.78	–	–	–	59BK
1 M $HClO_4$	25	2.52	–	–	–	–	–	61W
2 M $HClO_4$	25	2.51	–	–	–	–	–	61W
0	25	1.72	2.64	–	–	–	–	62AP
4 M $NaNO_3$	25	2.26	2.50	3.55	–	–	–	62F
0.5 M $HClO_4$	?	2.47	3.11	3.94	–	–	–	64VR
1.5 M $LiNO_3$	25	1.75	–	–	–	–	–	69M
1.5 M $NaNO_3$	25	2.49	4.03	3.53	–	–	–	69M
1.5 M KNO_3	25	2.66	4.40	4.91	–	–	–	69M
4 M $NaClO_4$	25	2.61	4.18	–	–	–	–	70H
3 M $NaClO_4$	25	2.58	3.84	4.2	–	−1.3	0.3	72Fa,b
4 M $NaClO_4$	20	2.70	3.25	4.15	3.35	–	–	75KB
4 M $Na(Cl,ClO_4)$	25	2.58	4.15	4.21	4.32	–	–	80H
1 M $(H,Li)ClO_4$	25	2.52	–	–	–	–	–	82T
0	25	2.75	4.37	5.0	–	−0.63	0.94	86BM
5 M $Na(Cl,ClO_4)$	25	2.64	3.99	4.45	3.59	–	–	94F

Sources: 55HH—calculated by Hepler and Hugus (1952) from the data of Moeller (1941); 53,54CV—Cozzi and Vivarelli (1953, 1954); 54CI—Carleson and Irving (1954); 54SE—Schufle and Eiland (1954); 54Sb—Sundén (1954b); 54Sc,d—Sundén (1954c,d); 58Z—Zelyanskaya et al. (1958); 59BK—Busaev and Kanaev (1959); 61W—White et al. (1961); 62AP—Altynov and Ptitsyn (1962); 62F—Fridman et al. (1962); 64VR—Vavra and Rudenko (1964); 69M—Mikhailova et al. (1969); 70H—Hasegawa (1970); 72Fa,b—Ferri (1972a,b); 75KB—Kondziela and Biernat (1975); 80H—Hasegawa et al. (1980); 82T—Tur'yan et al. (1982); 86BM—recommended values from critical review of Baes and Mesmer (1986); 94F—Ferri et al. (1994) (a recalculation of the data of Ferri (1972a) to higher ionic strength).

important, such that it is essentially the only species present at 350 °C.

Sverjensky et al. (1997) provide HKF equation parameters that permit the prediction of stability constants for the $InCl^+$ complex, based on thermodynamic data at 25 °C compiled by Turner et al. (1981) and correlation algorithms. The stability constant at 25 °C that is calculated from these parameters is log $\beta_1 = 3.26$, significantly different from the value log $\beta_1 = 2.75$ recommended by Baes and Mesmer (1986) and adopted in this study. Therefore, the HKF parameters of Sverjensky et al. (1997) should be used with caution.

Ferri (1972b) have reported stability constants for hydroxychloride complexes with the stoichiometries $InOHCl^+$ and In_2ClOH^{2+}. To our knowledge, stability constants for these species have not been determined in any other study. The dinuclear species In_2ClOH^{2+} is most likely of limited importance at the low total In concentrations probable in natural systems, but the mononuclear complex $InOHCl^+$ may be predominant under some conditions (see below). Baes and Mesmer (1986) estimated stability constants at infinite dilution for $InOHCl^+$ based on the data of Ferri (1972b) at 3 M ionic strength, and we adopt the former in this study.

4.5.4. Sulfate complexes

Stability constants for the complexes $InSO_4^+$ and $In(SO_4)_2^-$ are shown as a function of ionic strength in Fig. 10 and the details are given in Table 12. For both complexes, the agreement among the various studies is very good when account is taken of the differences in ionic strength. Our fits of Eq. (5) to both the β_1 and β_2 data result in values for these constants at infinite dilution that are essentially identical to those reported by Izatt et al. (1969). As stability constants determined by the latter authors for other metal–sulfate complexes seem to be reliable, we adopt their data for In–sulfate complexes in this review. Furthermore, Izatt et al. (1969) report enthalpies of complexation for these constants at infinite dilution which are required for extrapolation of the stability constants to higher temperatures.

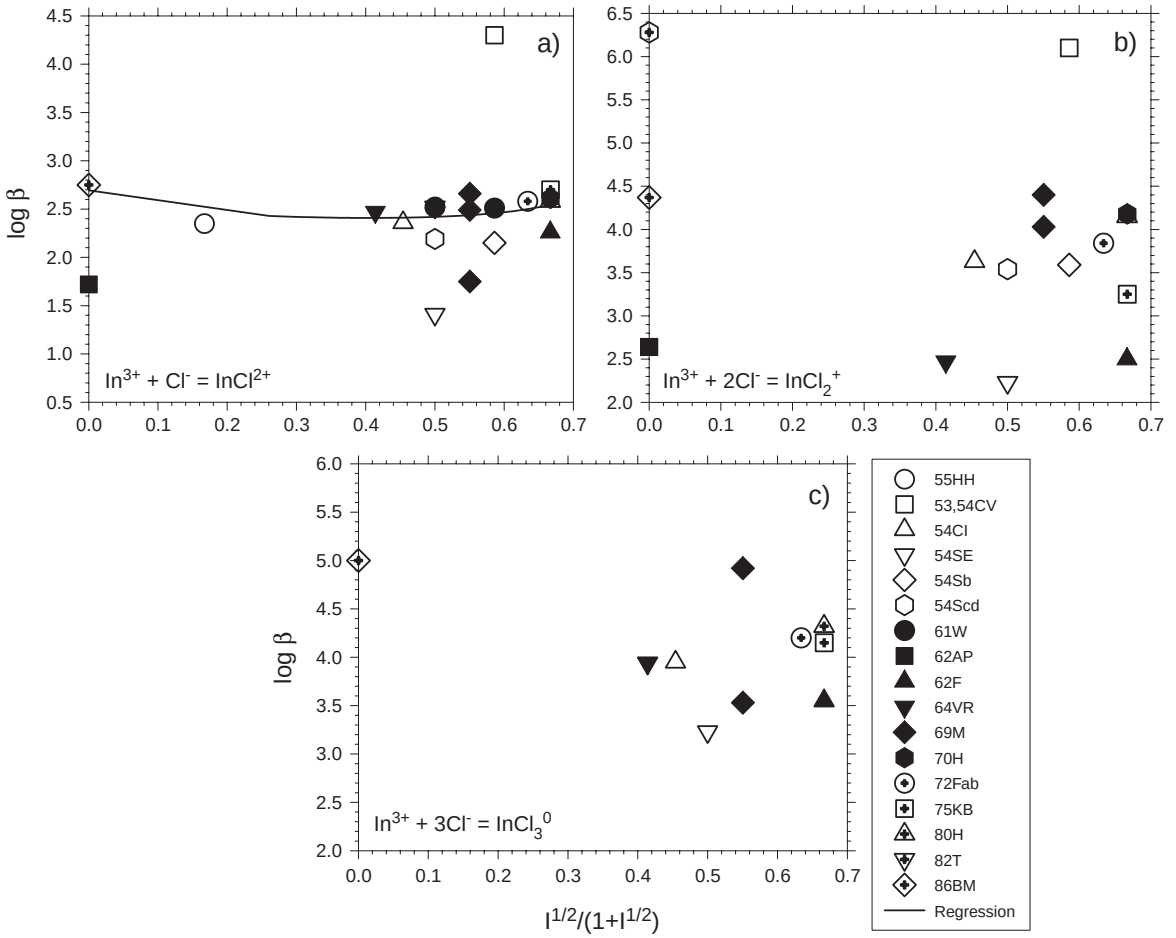

Fig. 9. Literature values of the stability constants for (a) $InCl^{2+}$; (b) $InCl_2^+$; and (c) $InCl_3^0$ vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 11.

4.5.5. Bisulfide complexes

Of the trivalent metal ions considered in this paper, In^{3+} is the softest and therefore the most likely to form stable bisulfide complexes. Tunaboylu and Schwarzenbach (1970) reported cumulative stability constants of log $\beta_1 = 10.5 \pm 1.3$ for $In(HS)^{2+}$ and log $\beta_2 = 17.1 \pm 1.4$ for $In(HS)_2^+$ at 25 °C in 1 M $NaClO_4$ solutions. These data imply that bisulfide forms the strongest complexes with In^{3+} of any of the ligands considered in this paper, with the exception of hydroxide. However, this does not necessarily mean that bisulfide complexes are the predominant means of In transport in hydrothermal solutions because other factors, such as relative ligand concentrations, pH and competition by metals for the various ligands are also important. In fact, in the section below on the solubility of In sulfide, it is seen that In–bisulfide complexes appear to play a relatively limited role, at least at 25 °C.

Sokolovskaya and Polyvyannyi (1980) interpret the results of measurements of the solubility of $NaInS_2$(s) in Na_2S–H_2O in terms of simple dissociation into the ions Na^+ and InS_2^-. If this interpretation is correct, then InS_2^- may need to be considered in sulfide-rich solutions, but there is currently a lack of thermodynamic data for this species.

4.5.6. Relative importance of hydroxide, fluoride and chloride complexes

In order to assess the relative importance of hydroxide, fluoride and chloride complexes in the transport of In, we have constructed a log a_{Cl^-} vs. pH diagram (Fig. 11) and a log a_{F^-} vs. pH diagram (Fig. 12), both at 25 °C and 1 bar. Fig. 11 shows that a substantial field of predominance exists for the hydroxychloride complex, $InOHCl^+$, at moderately acidic pH and a wide range of chloride activity. At pH >7, In–hydroxide complexes predominate at all reasonable chloride activities. How-

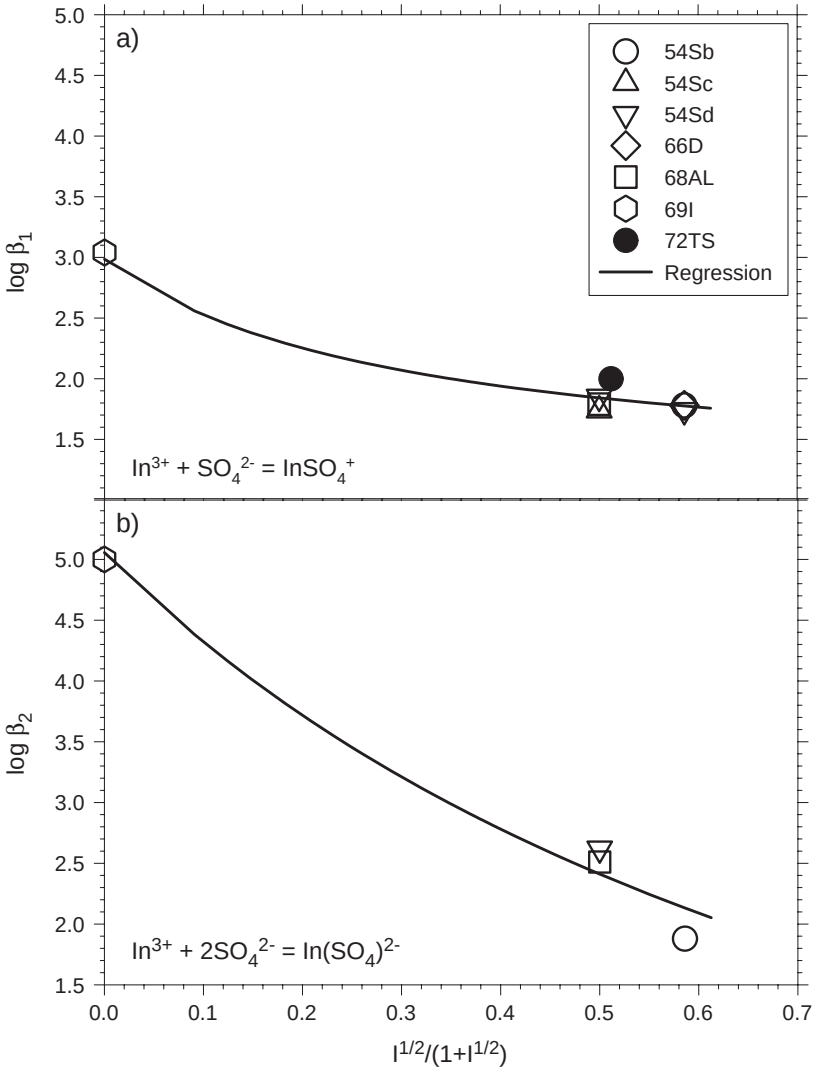

Fig. 10. Literature values of the stability constants for (a) $InSO_4^+$; and (b) $In(SO_4)_2^-$ vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 12.

ever, the neutral chloride complex, $InCl_3^0$, predominates from near-neutral to acidic pH at chloride activities greater than or equal to one. As noted above, In–chloride complexes with more than three chloride ions may well exist (e.g., $InCl_4^-$, $InCl_5^{2-}$), but stability constants for such species are poorly known and likely to be small.

Fluoride complexes predominate over the free In^{3+} ion at fluoride activities greater than 10^{-5} (Fig. 12). At a pH of 5, fluoride complexes predominate over hydroxide complexes of In at fluoride activities of greater than 10^{-3}. Thus, under acidic, fluoride-rich conditions, such as in greisens, fluoride complexes may play a role in the hydrothermal mass transfer of In, assuming that the relative stabilities of these complexes are comparable at elevated temperatures and pressures to those at the standard state. However, as pointed out by Wood (1992), free fluoride activities may be limited by solubility equilibria with fluorite or topaz and by competitive complexation of F^- by H^+, Na^+, Al^{3+}, etc. All these effects would need to be taken into account in quantitative modeling in order to assess the importance of transport of In as fluoride complexes in any given environment.

4.6. Scandium

Trivalent scandium is sometimes compared with Y^{3+} and the trivalent REE with respect to geochemical behavior. However, Sc^{3+} is substantially smaller than

Table 12
Summary of stability constants of In^{3+}–sulfate

Medium	Temperature (°C)	log β_n			
		$InSO_4^+$	$In(SO_4)_2^-$	$In(SO_4)_3^{3-}$	Source
2 M $NaClO_4$	20	1.78	1.88	2.45	54Sb
1 M $NaClO_4$	20	1.74	–	–	54Sc
1 M $NaClO_4$	20	1.85	2.62	3.02	54Sd
2 M $NaClO_4$	20	1.74	–	–	54Sd
0	30	3.74	–	–	62NA
2 M	?	1.78	–	–	66D
1 M $NaClO_4$	25	1.79	2.51	–	68AL
0	25	3.04	5.00	–	69I
1.1 M $NaClO_4$	25	2.0	–	–	72TS

Sources: 54Sb—Sundén (1954b); 54Sc—Sundén (1954c); 54Sd—Sundén (1954d); 62NA—Nanda and Aditya (1962); 66D—Deichman et al. (1966); 68AL—Aziz and Lyle (1968); 69I—Izatt et al. (1969); 72TS—Tur'yan and Strizhov (1972).

these other trivalent Group-3b and lanthanide cations. Moreover, Sc^{3+} appears to form much stronger complexes with ligands such as F^- and OH^- than does Y^{3+} or the REE (Grammaccioli et al., 1999, 2000), even when account is taken of its smaller size. Thermodynamic properties of aqueous complexes of Sc were reviewed previously by Travers et al. (1976).

Recent Raman spectroscopic measurements and ab initio molecular orbital calculations (Rudolph and Pye, 2000) indicate that the hydrated Sc^{3+} ion contains six water molecules in its primary hydration sphere. Thus, Sc^{3+} differs from the trivalent REE for which the weight of evidence (cf. Wood, 1990) suggests that the light and heavy REE have nine and eight waters of hydration, respectively. However, the lower coordination number for Sc^{3+} is consistent with its smaller size compared to the trivalent REE.

4.6.1. Hydroxide complexes

Values of K_{h11} for $ScOH^{2+}$ reported in the literature (Table 13) show reasonably good agreement when account is taken of ionic strength (Fig. 13a). In fact, if the data from Schweitzer and Winkley (1967) and Komissarova et al. (1971a) are excluded, a least-squares fit of a straight line to the remaining data shown in Fig. 13a results in no data deviating from the line by more than about ±0.3 log units. Moreover, the regression intercept is almost exactly the same as the value recommended by Baes and Mesmer (1986) at zero ionic strength, based on a critical review of the literature available up to 1976. Thus, it is concluded

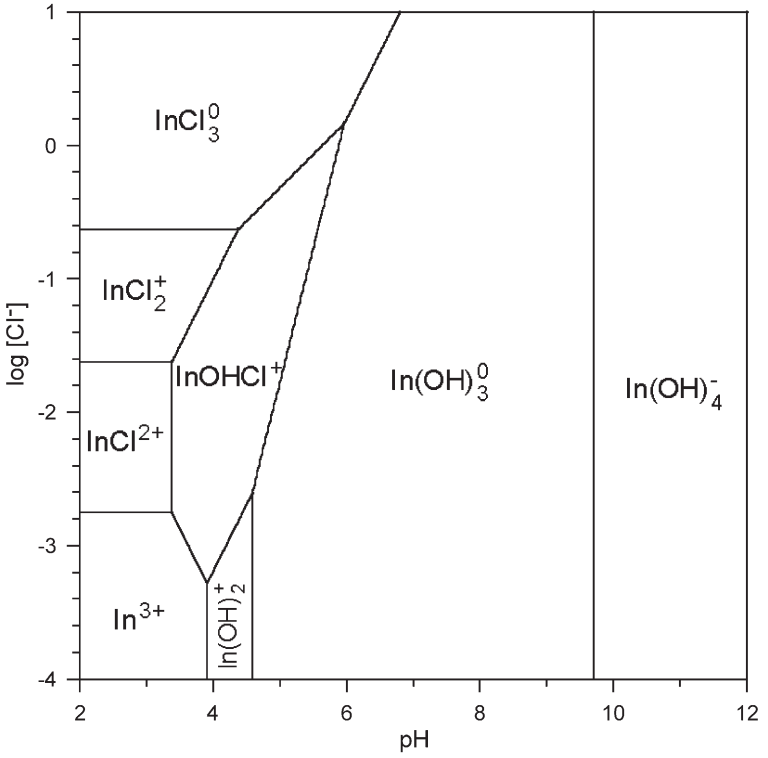

Fig. 11. Log a_{Cl^-} vs. pH diagram at 25 °C and 1 bar showing the fields of predominance of chloride, hydroxide and hydroxychloride complexes of In(III). This diagram is similar to the m_{Cl^-} vs. pH diagram published by Baes and Mesmer (1986), except the latter referred to a constant ionic strength of 3 M.

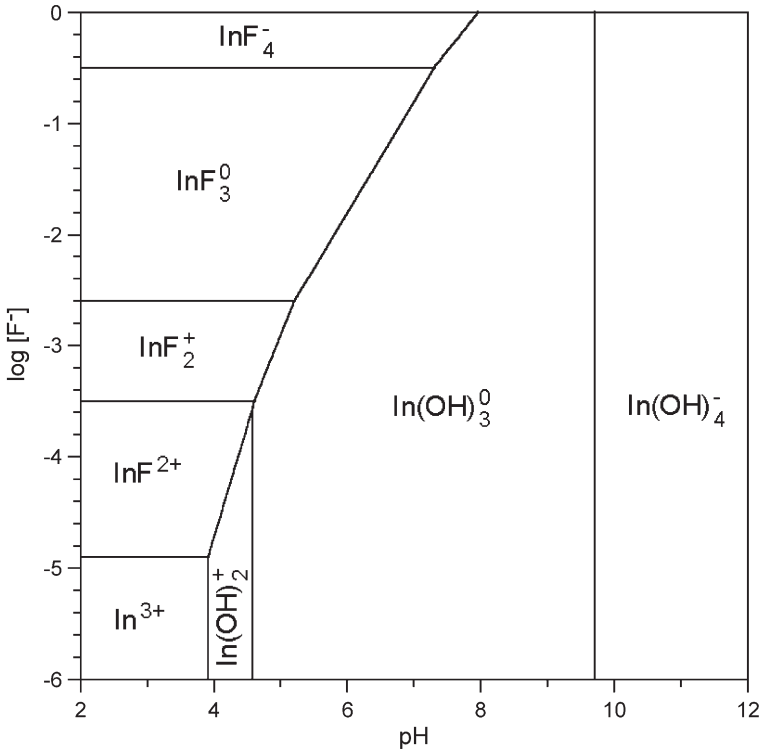

Fig. 12. Log a_{F^-} vs. pH diagram at 25 °C and 1 bar showing the fields of predominance of fluoride and hydroxide complexes of In(III).

that K_{h11} for $ScOH^{2+}$ is reasonably well known, and the value proposed by Baes and Mesmer (1986) remains the best estimate. There have been fewer measurements of K_{h12} and K_{h13}, and the agreement among the studies is relatively poor. Baes and Mesmer (1986) point out that the values of K_{h12} and K_{h13} determined by Antonovich and Nazarenko (1968) at 20 °C and 0.1 M ionic strength are theoretically reasonable. Moreover, the K_{h11} value of Antonovich and Nazarenko (1968) is in reasonable agreement with the regression line in Fig. 13a, and excellent agreement with the more recent measurement of Brown et al. (1983). Thus, we have no reason to suspect the values of Antonovich and Nazarenko (1968) for K_{h12} and K_{h13}, on which Baes and Mesmer (1986) based their recommended values at zero ionic strength (Fig. 13b, c). Baes and Mesmer (1986) also estimated a value of log $K_{h14}=-26$, based on the data of Ivanov-Emin et al. (1960, 1968) for the solubility of $Sc(OH)_3(s)$ in alkaline solutions.

To the authors' knowledge, no measurements of Sc hydrolysis at elevated temperatures have been carried out. Shock et al. (1997) used the estimates of the hydrolysis constants for $ScOH^{2+}$, $Sc(OH)_2^+$, $Sc(OH)_3^0$, $Sc(OH)_4^-$ (which they formulate as $ScOH^{2+}$, ScO^+, $HScO_2^0$ and ScO_2^-) from Baes and Mesmer (1986), together with correlation algorithms, to estimate parameters for the HKF equation for these species. These parameters permit estimation of the hydrolysis constants, but as there are no experimental measurements of Sc^{3+} hydrolysis at elevated temperatures and pressures, the accuracy of these estimates cannot be assessed. Fig. 14 shows the distribution of Sc–hydroxide complexes as a function of pH and temperature, based on hydrolysis constants estimated from HKF parameters given by Shock et al. (1997). At 25 °C, the hydrated Sc^{3+} ion predominates only at pH <4, whereas at 300 °C, unhydrolyzed Sc^{3+} is not predicted to be present in significant quantities, even at pH <1. The predominance field for $Sc(OH)_2^+$ is predicted to be very narrow at all temperatures. At geologically reasonable pH values, $Sc(OH)_3^0$ and $Sc(OH)_4^-$ are predicted to become increasingly important as temperature increases. However, as pointed out above, the HKF parameters of Shock et al. (1997) may overestimate the degree of hydrolysis of trivalent ions.

4.6.2. Fluoride complexes

As discussed by Grammaccioli et al. (1999, 2000), fluoride complexes may be of great importance in the hydrothermal transport of scandium. In fact, the stability constant of the first scandium fluoride complex

Table 13
Summary of Sc^{3+} hydrolysis constants from the literature

Medium	Temperature (°C)	log K_{hpq}			
		$ScOH^{2+}$	$Sc(OH)_2^+$	$Sc(OH)_3^0$	Source
1 M $NaClO_4$	25	−5.1	−10.22	–	56B
1 M $NaClO_4$	25	−5.18	–	–	66A
1 M $NaClO_4$	25	−5.15	–	–	66Aa
0.01 M $NaClO_4$	25	−3.82	–	–	67SW
0.1 M ClO_4^-	20	−4.9	−10.7	−17.3	68AN
0.1 M KNO_3	25	−4.47	–	–	71AO
1 M $NaClO_4$	25	−4.5	−9.9	−15.9	71K
1 M KNO_3	25	−4.4	−10.2	−15.4	71K
0.05 M $Na(Cl,ClO_4)$	25	−4.55	−8.76	–	72US
0.5 M $(H,Na)ClO_4$	22?	−5.0	–	–	80DG
0.1 M KNO_3	25	−4.84	–	–	83B
0	25	−4.3	−9.7	−16.1	86BM
1 M $NaClO_4$	10	−5.6	–	–	86BMa
1 M $NaClO_4$	40	−4.53	–	–	86BMa
0.5 M $NaClO_4$	25	−4.68	–	–	86BMa
0.1 M $NaClO_4$	25	−4.47	–	–	86BMa
0.01 M $NaClO_4$	25	−4.48	–	–	86BMa
0.001–0.01 M	25	−4.4	−9.5	–	96S

Sources: 56B—calculated from the data of Kilpatrick and Pokras (1954) by Biedermann et al. (1956); 66A—Aveston (1966); 66Aa—calculated by Aveston (1966) from the data of Kilpatrick and Pokras (1953); 67SW—Schweitzer and Winkley (1967). 68AN—Antonovich and Nazarenko (1968); 71AO—Akalin and Özer (1971); 71K—calculated from data of Komissarova et al. (1971a) (using log $K_w = -13.8$; Martell and Smith, 1998); 72US—Usherenko and Skorik (1972); 80DG—Davydov and Glazacheva (1980); 83B—Brown et al. (1983); 86BM—recommended values of Baes and Mesmer (1986); 86BMa—calculated from the data of Kilpatrick and Pokras (1954) by Baes and Mesmer (1986); 96S—Stryapkov et al. (1996).

(ScF^{2+}) is more than two orders of magnitude greater than would be expected based on a comparison to Y^{3+} and trivalent rare earth elements (REE).

Several measurements of the stability constants of scandium complexes have been carried out by a variety of methods, and these are in very good agreement (see summary in Table 14 and Fig. 15). The majority of the measurements have been made at 0.5 M ionic strength; only one study, that of Kury et al. (1959), provides values at infinite dilution. Therefore, an empirical extrapolation to infinite dilution is required. We fit Eq. (5) to the stability constant data for ScF^{2+}, ScF_2^+ and ScF_3^0 (Fig. 15) and it can be seen that the equation fits the data well. The values of log β at infinite dilution obtained for each of the Sc–fluoride complexes are within 0.1 to 0.3 log units of the equivalent values reported by Kury et al. (1959). Moreover, if the data of Kury et al. (1959) are excluded from the fit, the values of log β at infinite dilution obtained by regression of the remaining data are somewhat lower, but still within 0.2 to 0.5 log units of the results of Kury et al. (1959). Thus, we believe that the stability constants obtained from regression of the entire data set for each of the Sc–fluoride complexes are accurate to within 0.2 to 0.5 log units. These values are given in Table 14.

Apparently, no measurements of Sc–fluoride complex stability constants at elevated temperatures have been reported. However, enthalpies for reactions of the type:

$$Sc^{3+} + nHF^0 \leftrightarrow ScF_n^{3-n} + nH^+ \quad (7)$$

have been determined indirectly by Kury et al. (1959), based on the temperature dependence of equilibrium constants determined potentiometrically, and directly by Lundeen and Hugus (1992) via solution calorimetry. The values determined by these two methods also are in very good agreement (Table 15). In order to obtain the enthalpy for the complexation reactions:

$$Sc^{3+} + F^- \leftrightarrow ScF_n^{3-n} \quad (8)$$

it is necessary to subtract the enthalpy change for the reaction:

$$HF^0 \leftrightarrow H^+ + F^-. \quad (9)$$

This has been done by Ahrland (1967) to obtain a value of $\Delta H^\circ = 2.5$ kJ mol^{-1} for the reaction:

$$Sc^{3+} + F^- \leftrightarrow ScF^{2+}. \quad (10)$$

The endothermic enthalpy is consistent with scandium–fluoride complexation being a hard–hard interac-

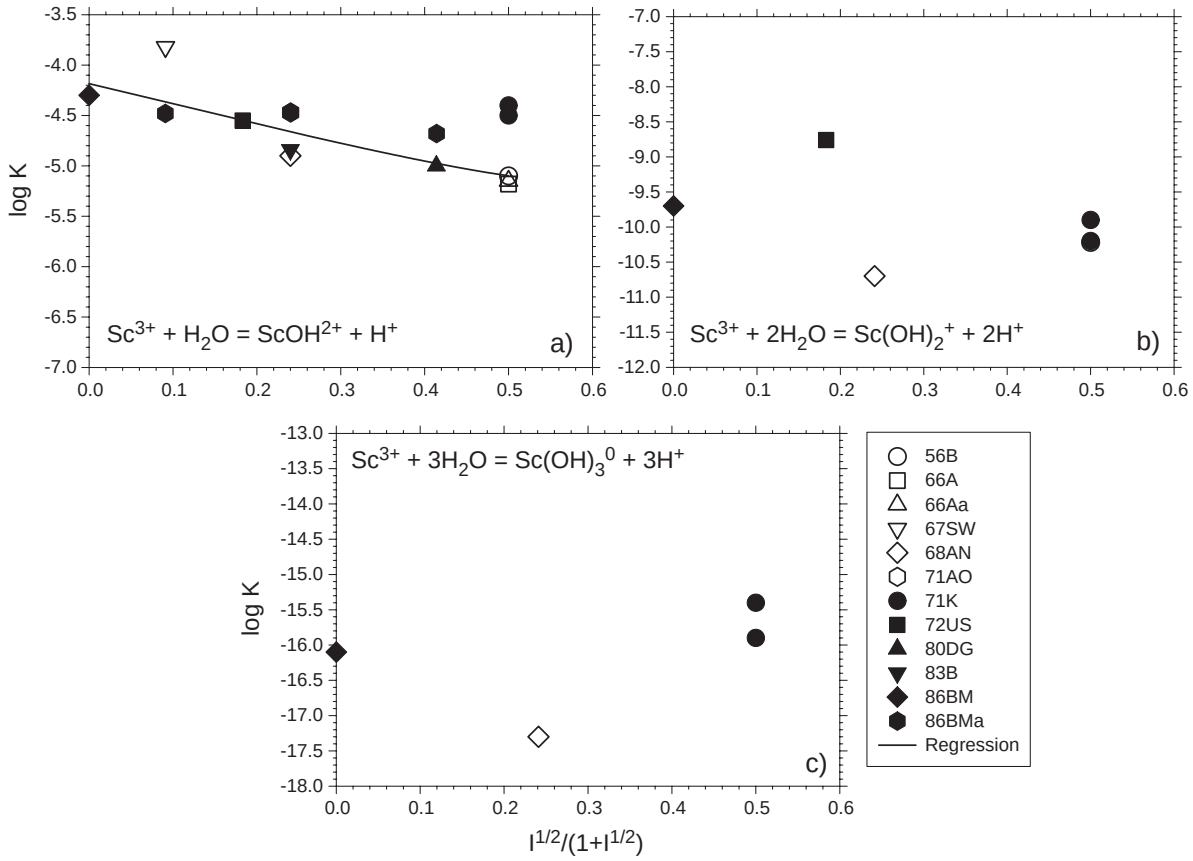

Fig. 13. Literature values of the hydrolysis constants for the species: (a) $ScOH^{2+}$; (b) $Sc(OH)_2^+$; and (c) $Sc(OH)_3^0$ vs. $I^{½}/(1+I^{½})$, where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 13.

tion in the Pearson (1963) sense, and indicates that the stability constants for scandium–fluoride complexes should increase monotonically with temperature.

4.6.3. Chloride complexes

As is the case with the trivalent REE (Wood, 1990), chloride complexes of Sc^{3+} are quite weak at 25 °C and, therefore, there is poor agreement among experimentally measured values of their stability constants (Table 16 and Fig. 16). Thus, at low temperatures it is expected that chloride complexes will play a relatively minor role in the mass transfer of scandium. On the other hand, experimental studies (Gammons et al., 1996) show that REE–chloride complexes become increasingly stable with increased temperature, such that they could play a role in hydrothermal mass transfer at temperatures above approximately 200 to 250 °C. It might therefore be anticipated that Sc–chloride complexes may behave in a similar manner, and the stability constants of these complexes should be determined at elevated temperatures.

4.6.4. Sulfate complexes

Sulfate complexes of the trivalent REE are moderately strong (Wood, 1990) so Sc–sulfate complexes should also be moderately strong. A handful of experimental measurements of the stability constants of Sc–sulfate complexes have been carried out at standard conditions (Table 17) and, although there is considerable scatter among the measurements (Fig. 17), it does appear as though Sc–sulfate complexes are stronger than Sc–chloride complexes, but weaker than Sc–fluoride and–hydroxide complexes. The value reported by Tateda (1965) for β_1 in 0.5 M $NaClO_4$ solutions appears to be too low compared to the values at infinite dilution given by Izatt et al. (1969) and at 1.0 M $NaClO_4$ by Belyavskaya et al. (1966). In their critical compilation of stability constants, Martell and Smith (1998) seem to have applied a correction to the value of β_1 of Tateda (1965) that brings it more in line with the other measurements, but no detailed explanation is given as to how the correction was made. Samodelov (1964) reported ap-

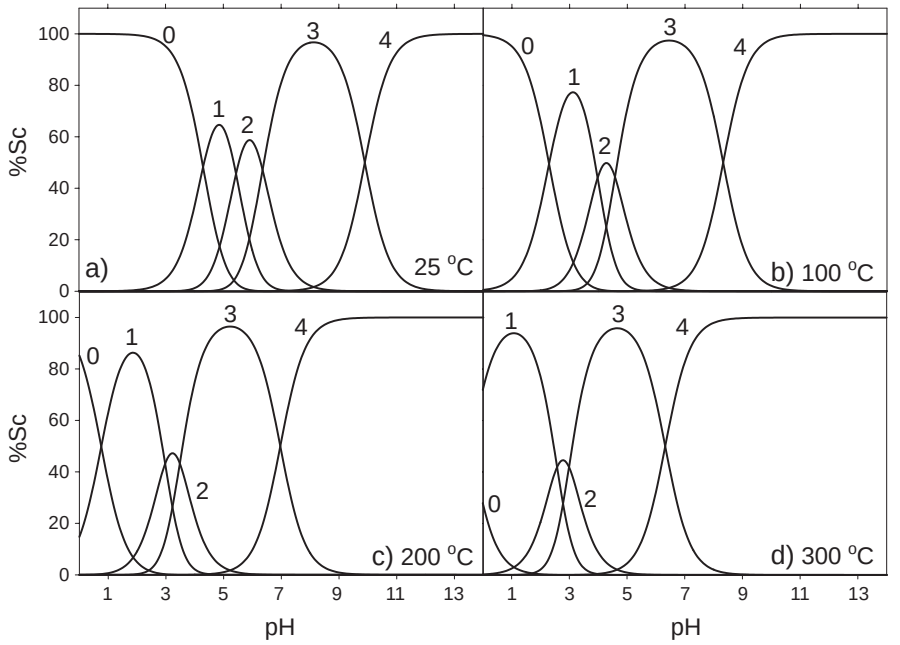

Fig. 14. The distribution of Sc^{3+}–hydroxide complexes as a function of pH at 25, 100, 200 and 300 °C at SWVP. The numbers correspond to the following species: 0—Sc^{3+}; 1—$ScOH^{2+}$; 2—$Sc(OH)_2^+$; 3—$Sc(OH)_3^0$; 4—$Sc(OH)_4^-$.

parent values of log $\beta_1 = 0.62$ and log $\beta_2 = 1.50$ at 2.0 M H_2SO_4, but given their magnitude, these lower values almost certainly refer to the reactions involving bisulfate ion:

$$Sc^{3+} + HSO_4^- \leftrightarrow ScSO_4^+ + H^+ \quad (11)$$

$$Sc^{3+} + 2HSO_4^- \leftrightarrow Sc(SO_4)_2^- + 2H^+ \quad (12)$$

rather than the reactions involving SO_4^{2-} to which the data in Table 17 refer. Because the stability constants that Izatt et al. (1969) obtained for REE–and Y–sulfate complexes agree reasonably well with the most reliable stability constants obtained in other studies, their values for the Sc–sulfate complexes should be reasonably reliable. Moreover, Izatt et al. (1969) also measured enthalpies of complexation for the first two Sc–sulfate complexes at infinite dilution, permitting extrapolation of their data to higher temperatures.

Table 14
Summary of stability constants from the literature for fluoride complexes of Sc^{3+}

Medium	Temperature (°C)	log β_n				
		ScF^{2+}	ScF_2^+	ScF_3^0	ScF_4^-	Source
0.5 M $NaClO_4$	25	6.19	11.47	15.55	18.40	59K
0	25	7.08	12.89	17.37	20.22	59K
0.5 M $NaClO_4$	25	6.17	11.44	15.46	18.49	69ALb
0.01–0.1 M $ScCl_3$	25	6.28	–	–	–	76I
0.5 M $NaClO_4$	25	6.18	11.52	15.8	–	80H
0.1 M KNO_3	25	6.22	11.52	15.47	–	87Y

Sources: 59K—Kury et al. (1959); 69ALb—Aziz and Lyle (1969b); 76I—Ivanov-Emin et al. (1976); 80H—Hancock et al. (1980); 87Y—Yuchi et al. (1987).

4.6.5. Relative importance of fluoride and hydroxide complexes

Fig. 18 is an activity–activity diagram depicting the fields of predominance of Sc–fluoride and –hydroxide complexes as a function of pH and free fluoride activity at 25 °C, 1 bar and infinite dilution. As is the case for In, fluoride complexes are predominant under acidic conditions at relatively low fluoride activities. However, as a consequence of the fact that the Sc fluoride complexes are stronger and the Sc hydroxide complexes are somewhat weaker than the corresponding complexes with In, fluoride complexes predominate over hydroxide complexes for Sc at lower fluoride activities and higher pH values than is the case for In. Thus, at least at 25 °C, fluoride complexes should be quite important for Sc transport at acid pH and geologically reasonable free fluoride activities, in accord with the qualitative conclusions of Grammaccioli et al. (1999, 2000).

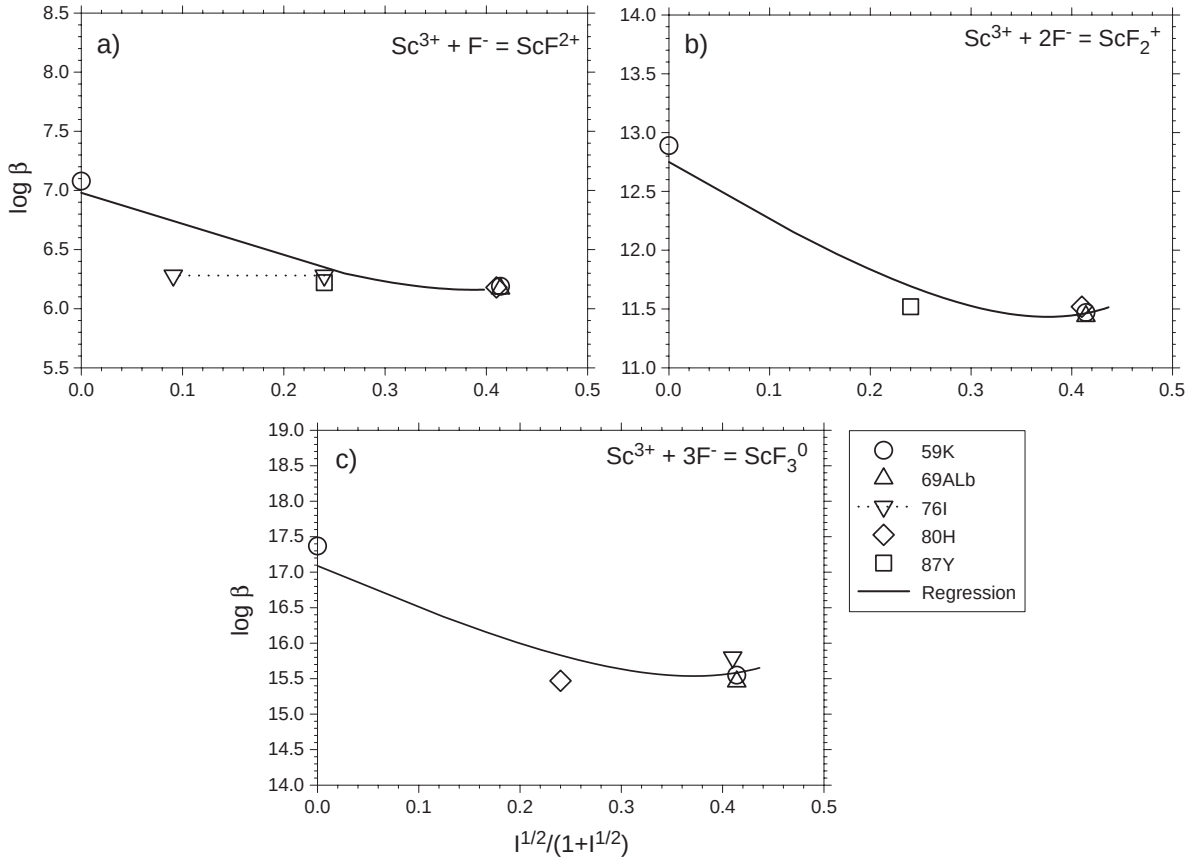

Fig. 15. Literature values of the stability constants for (a) ScF^{2+}; (b) ScF_2^+; (c) ScF_3^0; and (d) ScF_4^- vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 14.

4.7. Recommended values of hydrolysis and stability constants

In the preceding sections we have reviewed and assessed the available data on hydrolysis and stability constants for various complexes of Ga, Ge, In and Sc. On the basis of this assessment, we have provided, in Tables 18 and 19, recommended values for these constants at 25 °C, 1 bar and infinite dilution. The errors given in these tables represent our best estimates of the overall uncertainty in the recommended values based on the amount of published data and their degree of agreement. Where the existence of a species is in question, or the recommended equilibrium constant is based on a single study, the recommended value is followed by a question mark.

5. Solubilities of relevant solid phases

To fully constrain genetic models of supergene and hydrothermal deposits of Ga, Ge, In and Sc, it is necessary to be able to calculate the solubilities of minerals containing these metals. To accomplish the latter goal, in addition to stability constants of pertinent aqueous complexes, we must also have solubility products of relevant solid phases as a function of tempera-

Table 15
Comparison of measured enthalpies of reaction from the literature for the reaction: $Sc^{3+} + nHF^0 \leftrightarrow ScF_n^{3-n} + nH^+$

Medium	Temperature (°C)	ΔH (kJ mol^{-1})				
		ScF^{2+}	ScF_2^+	ScF_3^0	ScF_4^-	Source
0.5 M $NaClO_4$	25	−9.6 ± 4.2	−26.8 ± 8.4	−41.0 ± 13.4	–	59K
0.5 M $NaClO_4$	25	−9.0 ± 1.7	−27.5 ± 2.8	−42.0 ± 2.1	−91.7 ± 1.9	92LH

Sources: 59K—Kury et al. (1959); 92LH—Lundeen and Hugus (1992).

Table 16
Summary of stability constants from the literature for chloride complexes of Sc^{3+}

Medium	Temperature (°C)	log β_n				
		$ScCl^{2+}$	$ScCl_2^+$	$ScCl_3^0$	$ScCl_4^-$	Source
0.5 M $NaClO_4$	25	1.07	1.35	–	–	62P
0.691 M $HClO_4$	25	0.04	−0.12	–	–	64R
2 M	25?	0.14	0.54	–	–	64S
6 M	25?	1.45	0.70	−0.22	−0.37	64S
1 M	20	−0.80	–	0.16	–	65A
4.0 M $HClO_4$	25	−0.12	−0.84	−1.40	–	66SH

Sources: 62P—Paul (1962); 64R—Reed et al. (1964); 64S—Samodelov (1964); 65A—Alimarin et al. (1965); 66SH—Sekine and Hasegawa (1966).

ture and pressure. As noted in the Introduction, the metals of interest rarely occur in minerals in which they are essential constituents. Furthermore, solubility products are uniformly unavailable for most of the rare minerals in which Ga, Ge, In and Sc are essential components. To calculate the solubilities of these metals in solid solution with more common minerals, we require solubility products for the pure, end-member phase (commonly hypothetical) containing Ga, Ge, In or Sc, and a mixing model with which to calculate the activity of this end-member in the solid solution.

For example, suppose we wish to calculate the concentration of Ge in a solution in equilibrium with the solid solution $(Si,Ge)O_2$(quartz). In this case, we would require the equilibrium constant for the reaction:

$$GeO_2(\text{hexagonal}) + 2H_2O(l) \leftrightarrow H_4GeO_4^0 \quad (13)$$

where GeO_2(hexagonal) is the pure Ge end-member phase with a structure similar to that of quartz. For the above reaction we may write

$$K = \frac{a_{H_4GeO_4^0}}{a^{qtz}_{GeO_2} a^2_{H_2O}}. \quad (14)$$

The activity term for liquid water can be taken to be unity in most cases, but if we define the standard state to be pure GeO_2(hexagonal), then the term for the activity of GeO_2 in solid solution with quartz could be quite different from unity. To calculate this activity, we would need information on the mixing properties between GeO_2 and SiO_2, unless the solid solution can be taken to be ideal, and the solubility product for the pure end member phase. In some cases, the pure end-member phase might not actually be stable, e.g., Ge in solid solution in sphalerite, where the Ge end-member would be a hypothetical Ge-bearing sulfide with the sphalerite structure. In this case, direct experimental measurements of the solubility product of the end-member phase are impossible. In general, the solubility products for most of the end-member phases of interest here are not available.

In this section, we critically review solubility product data for some solids containing Ga, Ge, In or Sc for which data are available in the literature. The solids included represent either potential end-members of likely solid solutions or phases that, although rare, do occur naturally and may place an upper boundary on the concentrations of the metals of interest in natural aqueous solutions.

5.1. Notation

We employ the following notation for solubility reactions. For the general dissolution reaction for a metal hydroxide written as

$$M(OH)_q(s) \leftrightarrow M^{+q} + qOH^- \quad (15)$$

we write the solubility product as

$$K_{s0} = a_{M^{+q}} a^q_{OH^-}. \quad (16)$$

The solubility of a hydroxide is also often expressed as

$$M(OH)_q(s) + qH^+ \leftrightarrow M^{+q} + qH_2O(l) \quad (17)$$

for which the equilibrium constant is written

$$K^*_{s0} = \frac{a_{M^{+q}}}{a^q_{H^+}}. \quad (18)$$

The generalized dissolution reaction for sulfide phases is

$$M_pS_q \leftrightarrow pM^{+2q/p} + qS^{2-} \quad (19)$$

and the solubility product is

$$K_{s0} = a^p_{M^{+2q/p}} a^q_{S^{2-}}. \quad (20)$$

5.2. Gallium

A gallium phase for which there are data on solubility over a comparatively wide range of temperatures is α-GaOOH(s). This phase is relevant to the occurrence of Ga in bauxites and may also represent an end-member for Ga substitution in oxyhydroxide phases such as goethite or boehmite. Recently, Bénézeth et al. (1997) and Diakonov et al. (1997) measured the solubility of this phase up to 250 °C and provided HKF-equation parameters to calculate the solubility product up to 350 °C. Pokrovski et al. (1997) provide

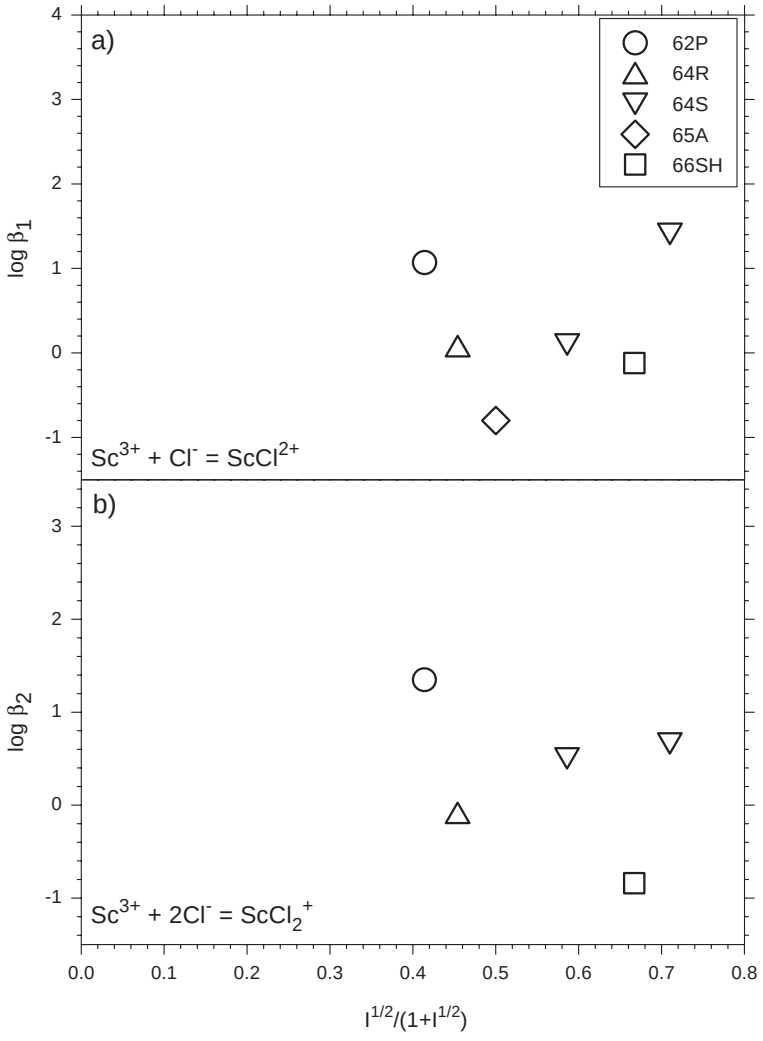

Fig. 16. Literature values of the stability constants for (a) $ScCl^{2+}$and (b) $ScCl_2^+$ vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 16.

thermodynamic data (Gibbs free energies of formation, enthalpies, heat capacities, etc.) for α-GaOOH(s) up to 700 K. The solubility of α-GaOOH(s) also was measured up to 100 °C recently by Uchida and Okuwaki (1997). These and older determinations of the equilibrium constant for the reaction

$$\alpha - \mathrm{GaOOH(s)} + 3\mathrm{H^+} \leftrightarrow \mathrm{Ga^{3+}} + 2\mathrm{H_2O(l)} \qquad (21)$$

are given in Table 20. Reported equilibrium constants for this reaction at zero ionic strength are plotted as a function of temperature in Fig. 19. There is some disagreement among the values shown in this figure with many of the older measurements being higher than the equilibrium constants calculated using the HKF equation parameters of Bénézeth et al. (1997). The latter authors suggest that many of the earlier studies may have suffered from the presence of the more soluble $Ga(OH)_3$(s) resulting in overestimation of the equilibrium constant. The value obtained by Uchida and Okuwaki (1997) at 100 °C is 0.6 log units smaller than the value predicted by Bénézeth et al. (1997), thus additional measurements to resolve this discrepancy are desirable. In the meantime, because the measurements of Bénézeth et al. (1997) and Diakonov et al. (1997) are the most comprehensive available and appear to have been very carefully done, we recommend the solubility products of α-GaOOH(s) calculated from their HKF equation parameters.

Solubilities of α-GaOOH(s) at zero ionic strength, calculated from the thermodynamic data in Bénézeth et al. (1997) and Diakonov et al. (1997), are depicted in Fig. 20. At 25 °C, the minimum is rather sharp and

Table 17
Summary of stability constants from the literature for sulfate complexes of Sc^{3+}

Medium	Temperature (°C)	log β_n			
		$ScSO_4^+$	$Sc(SO_4)_2^-$	$Sc(SO_4)_3^{3-}$	Source
10.5 M $NaClO_4$	25	1.66	3.04	4.0	65T
1.0 M $NaClO_4$	20	2.57	–	–	66B
0	25	4.04	5.70	–	69I
0	25	4.18	5.6	–	98MSa
0.5 M $NaClO_4$	25	2.59	4.0	–	98MSb

Sources: 65T—Tateda (1965); 66B—Belyavskaya et al. (1966); 69I—Izatt et al. (1969); 98MSa—listed by Martell and Smith (1998), apparently based on the data from Izatt et al. (1969); 98MSb—listed by Martell and Smith (1998), apparently based on the data of Tateda (1965).

occurs at about $10^{-9.3}$ m (~0.03 ppb). Moreover, although the solubility increases with both increasing and decreasing pH, it remains below 10^{-6} m from pH 3 to pH 8. The solubility of α-GaOOH(s) is lower than the solubilities of similar In and Sc oxyhydroxide phases (see below). With increasing temperature, solubility generally increases such that at 300 °C the solubility minimum occurs at approximately $10^{-5.5}$ m (~220 ppb). The solubility minimum also tends to become broader with increasing temperature which reflects the increased predominance of $Ga(OH)_3^0$ as shown in Fig. 3. Over much of the geologically reasonable pH range at 300 °C, $Ga(OH)_4^-$ is the predominant species, and at this temperature, the solubility increases to 10^{-4} m (~7 ppm) at pH = 6.

As discussed above, the only inorganic ligand besides hydroxide that is likely to contribute substantially to Ga transport is fluoride. Thus, in the absence of fluoride or possibly organic ligands, Ga solubility will be quite low at low temperatures, unless the pH is either unusually

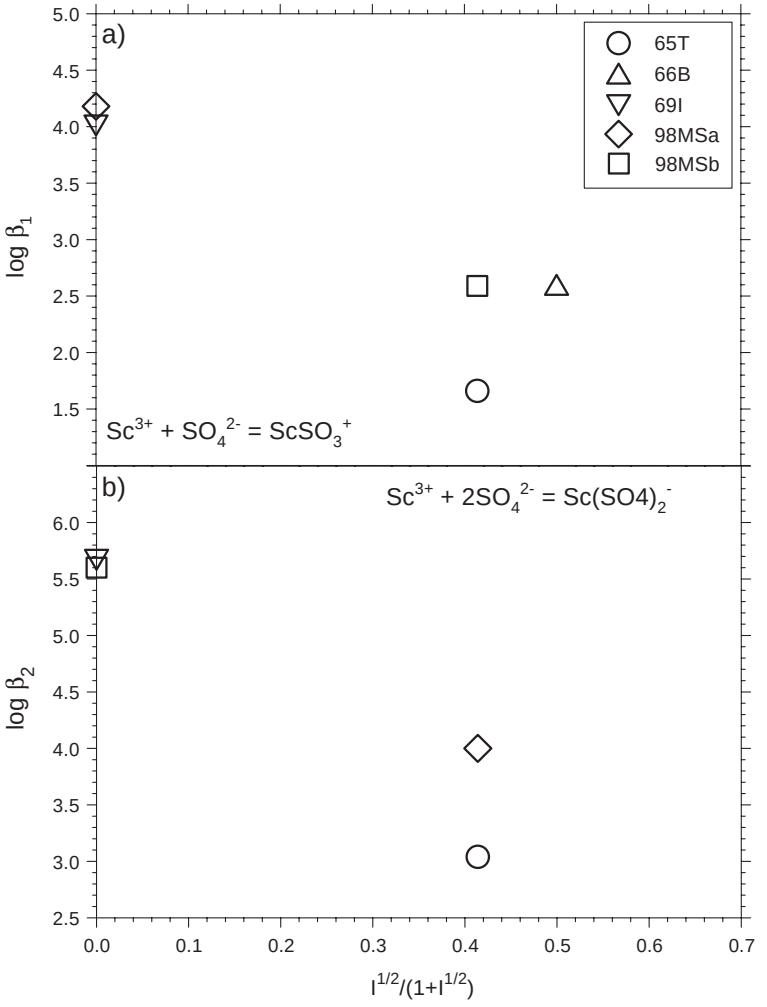

Fig. 17. Literature values of the stability constants for (a) $ScSO_4^+$; and (b) $Sc(SO_4)_2^-$ vs. $I^{½}/(1+I^{½})$ where I is ionic strength. The data are for 20–25 °C. Details regarding the sources of the data are given in the footnote to Table 17.

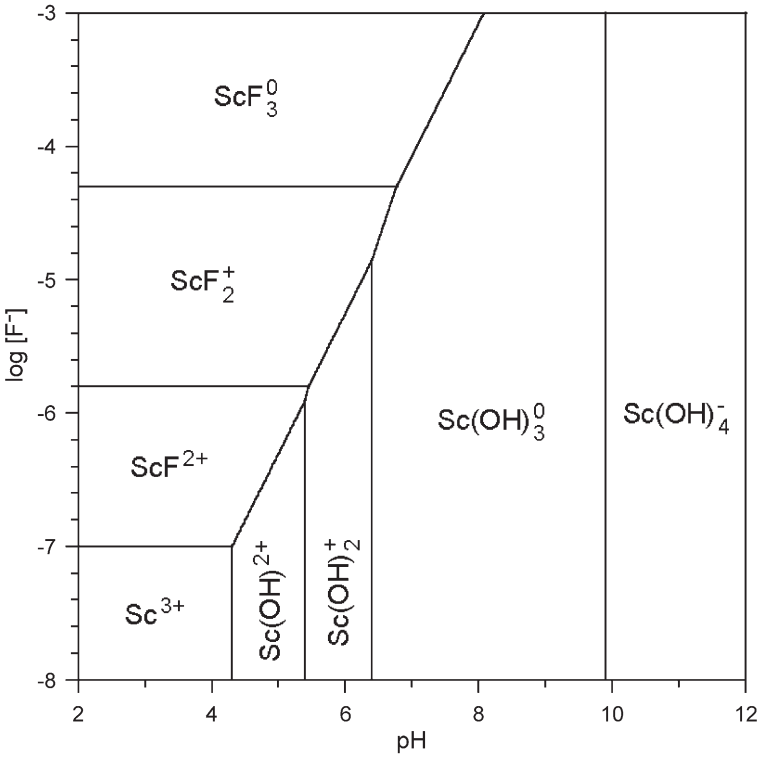

Fig. 18. Log a_{F^-} vs. pH diagram at 25 °C and 1 bar showing the fields of predominance of fluoride and hydroxide complexes of Sc(III).

acidic or unusually basic. On the other hand, the solubility increases significantly with increasing temperature. If Ga occurs as a minor substituent in an Al– or Fe–oxyhydroxide phase, then the concentration of Ga in solution in equilibrium with such a phase will be even lower (possibly by many orders of magnitude) than those depicted in Fig. 20. This can be understood with reference to reaction (21). A decrease in the activity of α-GaOOH(s) requires a correspondingly lower activity of dissolved Ga species. The relative immobility of Ga in weathering environments and its enrichment in bauxites is reflective of the low solubility of α-GaOOH(s) at 25 °C in the absence of complexing ligands other than water. Relatively low solubilities of Ga in the absence of fluoride are also consistent with the comparatively low Ga concentrations determined in geothermal waters.

Table 18
Recommended values of hydrolysis constants for Ga^{3+}, In^{3+}, and Sc^{3+}at 25 °C, 1 bar and infinite dilution

Species	log K_{h1n}	Species	log K_{h1n}	Species
$GaOH^{2+}$	−2.9 ± 0.3	$InOH^{2+}$	−4.0 ± 0.2	$ScOH^{2+}$
$Ga(OH)_2^+$	−7.3 ± 1.0	$In(OH)_2^+$	−7.8 ± 0.3	$Sc(OH)_2^+$
$Ga(OH)_3^0$	−11.9 ± 2.0	$In(OH)_3^0$	−12.4 ± 0.5	$Sc(OH)_3^0$
$Ga(OH)_4^-$	−15.7 ± 2.0	$In(OH)_4^-$	−22.1?	$Sc(OH)_4^-$

See text for comments.

Another Ga phase for which there are solubility data at elevated temperatures is $GaPO_4$(s). The solubility product at 25 °C (log K_{s0} = −21) was determined by Tananaev and Chudinova (1964) and the solubility in H_3PO_4 and H_2SO_4 solutions was determined at 150 to 260 °C by Motchany et al. (2000). The latter authors found that the solubility of $GaPO_4$(s) is retrograde (i.e., decreases with increasing temperature) over the temperature range investigated. We have been unable to find any reports of the natural occurrence of $GaPO_4$(s). Our calculations show that, given the solubility pro-

Table 19
Recommended values of stability constants for complexes of Ga^{3+}, In^{3+}, and Sc^{3+}at 25 °C, 1 bar and infinite dilution

Complex	log β	Complex	log β
GaF^{2+}	5.1 ± 0.5	$InCl_3^0$	5.0 ± 0.3
$GaSO_4^+$	2.8 ± 0.1	$InOHCl^+$	−0.63 ± 0.2
$Ga(SO_4)_2^-$	5.1 ± 0.2	$InSO_4^+$	3.0 ± 0.1
InF^{2+}	4.9 ± 0.3	$In(SO_4)_2^-$	5.0 ± 0.2
InF_2^+	8.4 ± 0.4	ScF^{2+}	7.0 ± 0.2
InF_3^0	11 ± 1	ScF_2^+	12.8 ± 0.3
InF_4^-	11.5?	ScF_3^0	17.1 ± 0.4
$InCl^{2+}$	2.75 ± 0.1	$Sc(SO_4)^+$	4.04 ± 0.1
$InCl_2^+$	4.37 ± 0.3	$Sc(SO_4)_2^-$	5.70 ± 0.2

See text for comments.

Table 20
Summary of solubility products of GaOOH(s) from the literature

Medium	Temperature (°C)	log $*K_{s0}$	Source
0	25	2.9	63FS, 86BM
3 m $NaClO_4$	60	3.66	67GS
1 M $NaClO_4$	50	3.7	69CT
Dilute	50	3.2	69CT
1 M $NaClO_4$	75	2.8	69CT
Dilute	75	2.2	69CT
1 M $NaClO_4$	50	4.29	71G
0	100	−0.60	97UO
0	150	−0.70	97B

Sources: 63FS—calculated by Feitknecht and Schindler (1963) from the data of Fetter (1957) and adopted by Baes and Mesmer (1986); 67GS—Gamsjäger and Schindler (1967); 71G—Gimblett (1971); 86BM—Baes and Mesmer (1986); 97UO—Uchida and Okuwaki (1997); 97B—Bénézeth et al. (1997).

ducts at 25 °C quoted above for $GaPO_4$(s) and α-GaOOH(s), the latter phase is far less soluble, and hence more stable, than the former phase at reasonable total phosphate concentrations over the pH range from 0 to 14. Because the solubility products of these two Ga phases both apparently decrease with increasing temperature (up to at least 250 to 300 °C), it seems likely that $GaPO_4$(s) remains the more soluble phase as temperature increases.

5.3. Germanium

Two polymorphs of GeO_2(s) are known: a more soluble polymorph with a hexagonal structure and a less soluble (more stable) polymorph with a tetragonal structure. Thermodynamic data (i.e., enthalpy, Gibbs free energy of formation and entropy) for the tetragonal polymorph are given by Faktor and Carasso (1965). The solubilities of these phases are frequently expressed via a reaction of the type

$$GeO_2(s) + 2H_2O(l) \leftrightarrow H_4GeO_4^0. \quad (22)$$

Measurements of the equilibrium constant for this reaction for both the hexagonal and tetragonal form are given in Table 21 and shown in Fig. 21. The data for the hexagonal polymorph are in excellent agreement, and from 0 to 100 °C conform to the equation

$$\log K = 0.8114 - 644.6/T(\mathrm{K}). \quad (23)$$

The data for the tetragonal polymorph extend over a wider temperature range (up to 350 °C), but the agreement among the various studies is somewhat poorer, although the discrepancies diminish with increasing temperature. We accept the recent values of Pokrovski and Schott (1998) as the most reliable. Their equilibrium constants are fit adequately by the equation

$$\log K = 1.5276 - 1975.2/T(\mathrm{K}). \quad (24)$$

The solubility of GeO_2(tet) is plotted as a function of temperature and pH in Fig. 22. As is the case with SiO_2, the solubility of GeO_2 is independent of pH in the range typical of most geologic environments (i.e., pH<8). Thus, in most cases, the predominant species will be $H_4GeO_4^0$. The pH at which $H_3GeO_4^-$ becomes important shifts somewhat towards lower pH up to

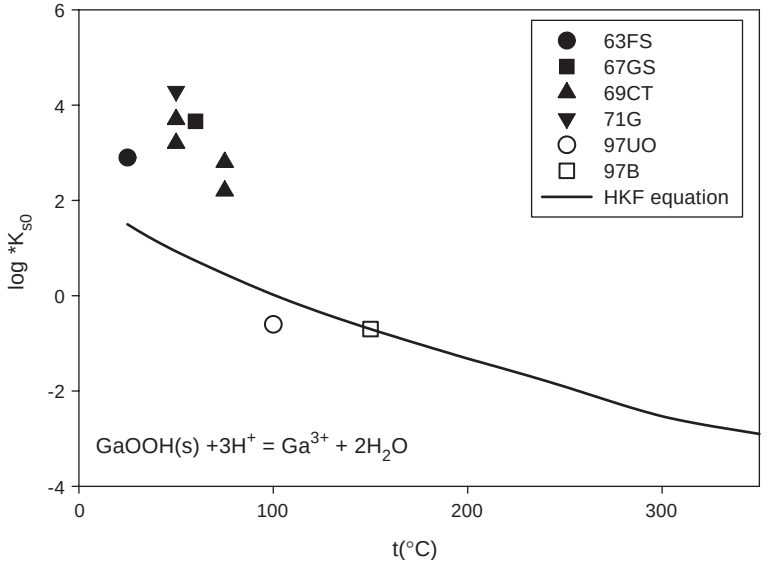

Fig. 19. Literature values for the solubility product of α-GaOOH as a function of temperature at infinite dilution and SWVP. The curve represents solubility products calculated from the HKF parameters given by Bénézeth et al. (1997).

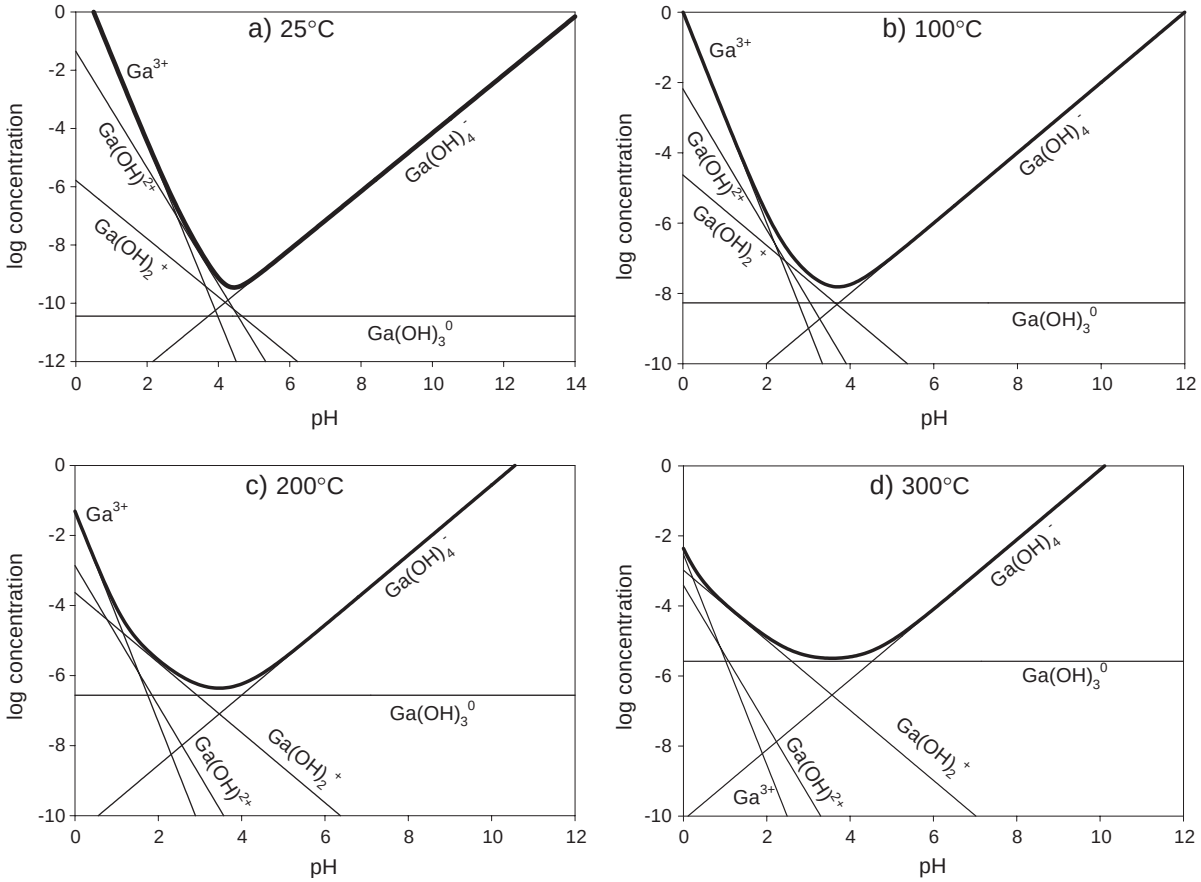

Fig. 20. Solubility of α-GaOOH vs. pH at zero ionic strength, SWVP and: (a) 25 °C; (b) 100 °C; (c) 200 °C; (d) 300 °C. Based on data given by Bénézeth et al. (1997).

200 °C (the limit of measured data), but with further increases in temperature, it is expected that this pH will minimize and then increase again. Indeed, the data of Pokrovski and Schott (1998) suggest that the minimum crossover pH occurs at 175 to 200 °C. Also similar to silica, the total solubility of GeO_2 increases with temperature. The solubility increases by more than 2 orders of magnitude between 25 and 200 °C. The solubility of pure GeO_2(tet) can be quite substantial (e.g., ~80 ppm at 200 °C). However, as discussed for Ga, the actual concentrations of Ge in most hydrothermal solutions would be much lower owing to the fact that Ge more often occurs as a minor substituent in solid solutions.

The solubility of the hexagonal polymorph is much higher than that of the tetragonal polymorph (>4 orders of magnitude at 25 °C). Thus, the tetragonal polymorph would be the stable pure GeO_2(s) phase in nature. However, when Ge occurs in solid solution in quartz, the thermodynamics of the hexagonal phase are most relevant to solubility calculations.

5.4. Indium

We include data on the solubility product of $In(OH)_3$(s) in this review because it does occur as the rare mineral dzhalindite. Moreover, this phase could represent an end-member of a solid solution series with other hydroxides, and its solubility provides a maximum limit to the concentrations of In possible in aqueous solutions. The solubility products in the literature are summarized in Table 22. Early estimates of the solubility of this phase probably relate to amorphous or poorly crystalline $In(OH)_3$(s). Aksel'rud and Spivakovskii (1959) made their measurements on precipitates aged for 76 days, and Baes and Mesmer (1986) have adopted their solubility product. More recent solubility measurements by Kochetkova et al. (1991) result in a solubility product three orders of magnitude lower than that obtained by Aksel'rud and Spivakovskii (1959). In the experiments of Kochetkova et al. (1991), $In(OH)_3$(s) was precipitated from an acidic solution of In–chloride by the

Table 21
Summary of equilibrium constants from the literature for the reaction: $GeO_2 + 2H_2O(l) \leftrightarrow H_4GeO_4^0$

Polymorph	Temperature (°C)	log *K*	Source
Hexagonal			
	25	−1.37	26M
	25	−1.37	29P
	11	−1.42	31SH
	20	−1.39	31SH
	26	−1.35	31SH
	35	−1.28	31SH
	41	−1.23	31SH
	25	−1.36	32LM
	40	−1.22	63EK
	60	−1.12	63EK
	80	−1.01	63EK
	100	−0.94	63EK
	25	−1.38	64GZ
	0	−1.59	64V
	25	−1.32	64V
	50	−1.14	64V
	75	−1.03	64V
	100	−0.94	64V
Tetragonal			
	25	−4.37	26M
	25	−5.34	87K
	50	−4.54	87K
	100	−3.42	87K
	160	−2.60	87K
	190	−2.35	87K
	250	−1.96	87K
	300	−1.77	87K
	25	−4.23	88KD
	100	−3.35	88KD
	160	−2.69	88KD
	190	−2.43	88KD
	250	−1.99	88KD
	300	−1.69	88KD
	25	−5.02	98PS
	50	−4.57	98PS
	90	−3.96	98PS
	150	−3.26	98PS
	200	−2.76	98PS
	250	−2.16	98PS
	300	−1.78	98PS
	350	−1.68	98PS

Sources: 26M—Müller (1926); 29P—Pugh (1929); 31SH—Schwarz and Huf (1931); 32LM—Laubengayer and Morton (1932); 63K—Evdokimov and Kogan (1963); 64GZ—Gayer and Zajicek (1964); 64V—Vehov et al. (1964); 87K—Kosova et al. (1987); 88KD—Kosova and Dem'yanets (1988); 98PS—Pokrovski and Schott (1998).

addition of calcium carbonate and the solution was equilibrated with the solid for more than 5 months. It is possible that this longer aging time resulted in an even more insoluble, well-crystallized solid hydroxide than was the case in the experiments of Aksel'rud and Spivakovskii (1959). However, the presence of carbonate in this system raises the possibility that a less soluble In–hydroxycarbonate or –carbonate phase was formed, explaining the lower solubility product. Such a problem appears to occur in solubility measurements of $Nd(OH)_3(s)$ and other REE hydroxides (cf. Wood et al., 2002). We therefore accept the solubility product determined by Aksel'rud and Spivakovskii (1959) as the best available estimate.

The solubility of $In(OH)_3(s)$ in pure water at 25 °C is plotted as a function of pH in Fig. 23, where it can be seen that this phase has a broad solubility minimum that ranges from pH ~4.5 to pH ~9. The concentration at the minimum is $10^{-7.3}$ mol L^{-1} or about 5 μg L^{-1} (ppb). The formation of more stable solid phases, or incorporation of In into a solid solution with another hydroxide phase, would lower the solubility even further. Thus, it is clear that, at least at low temperatures, strong complexation or acidic conditions, or both, are required to transport significant quantities of In.

As noted in the Introduction, In occasionally occurs as rare sulfide minerals in which it is an essential constituent, but more often it occurs as a trace component in more common sulfides such as sphalerite, chalcopyrite, stannite, etc. Thus, knowledge of the solubilities of various In–sulfide phases is required to fully understand the behavior of indium in hydrothermal systems. Unfortunately, the only In–sulfide phase for which solubility products are available is $In_2S_3(s)$, which has apparently not been reported to occur in nature. Because of the lack of data on other possibly more relevant In–sulfide phases, we have calculated the solubility of $In_2S_3(s)$ below to obtain at least some idea of how the presence of sulfur would affect the mobility of indium in aqueous solutions.

Reported solubility products for $In_2S_3(s)$, i.e., equilibrium constants for the reaction

$$In_2S_3(s) \leftrightarrow 2In^{3+} + 3S^{2-} \quad (25)$$

vary over a considerable range (Table 23). As stated above, Tunaboylu and Schwarzenbach (1970) provide the only values of stability constants for In(III)–bisulfide available. We have therefore used their stability constants and solubility product for $In_2S_3(s)$, determined at 20 °C and 1 M ionic strength, to calculate the solubility of $In_2S_3(s)$ in sulfide solutions as a function of pH and total dissolved sulfide concentration. For this calculation, we also required hydrolysis constants for In–hydroxide complexes at 1 M ionic strength, which were estimated using the parameters given by

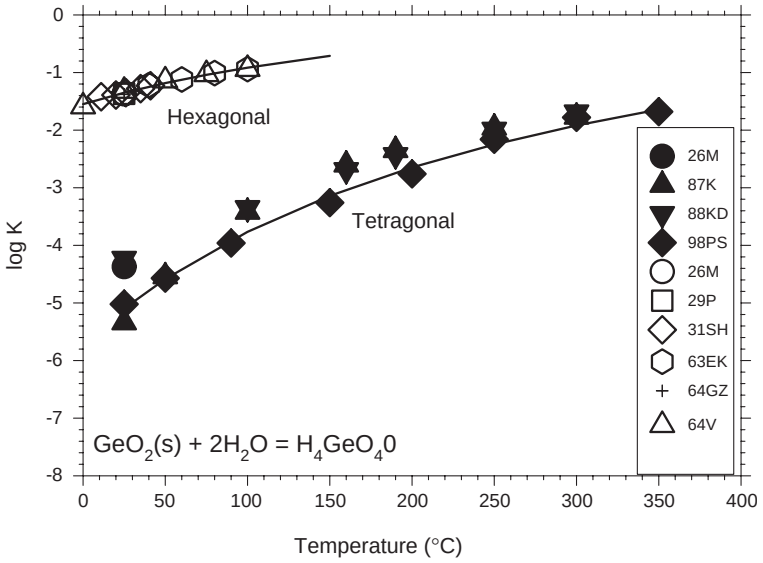

Fig. 21. Literature values for the equilibrium constants for the dissolution reactions of hexagonal and tetragonal GeO_2 as a function of temperature at SWVP. The regression lines are discussed in the text.

Baes and Mesmer (1986). Thus, the total solubility of $In_2S_3(s)$ is given by the expression:

$$[In]_T = [In^{3+}] + [In(HS)^{2+}] + [In(HS)_2^+] + [In(OH)^{2+}] + [In(OH)_2^+] + [In(OH)_3^0] + [In(OH)_4^-]$$

where the brackets denote concentration. The results of this calculation are depicted for two different values of total dissolved sulfide in Fig. 24.

A comparison of Fig. 24 with Fig. 23 reveals that, even allowing for differences in the ionic strengths employed to calculate these diagrams, the solubility of $In_2S_3(s)$ is considerably lower than that of $In(OH)_3(s)$. Although bisulfide complexes are formed and do increase the solubility of $In_2S_3(s)$ in the pH range from ~3 to ~8 above that contributed by In^{3+} and In–hydroxide complexes alone, they are not strong enough to overcome the greater stability of the sulfide phase with respect to dissolution. Thus, at least at low temperatures,

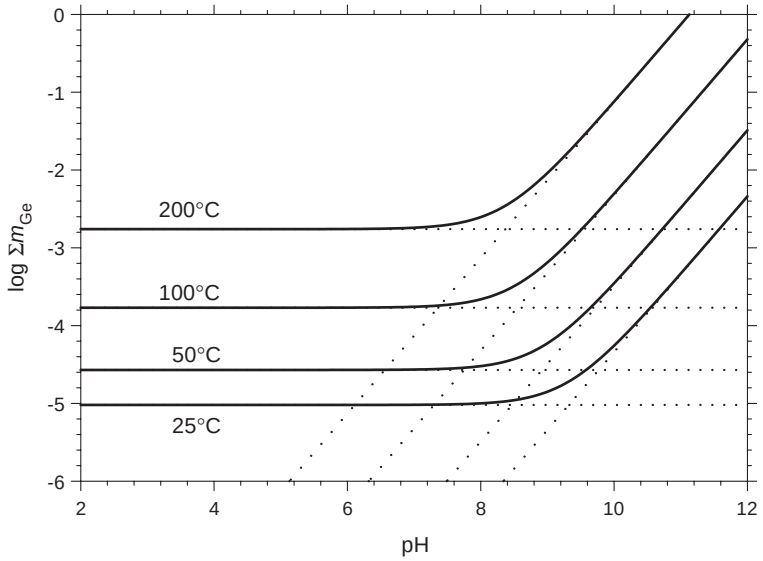

Fig. 22. The solubility of GeO_2(tet) as a function of pH and temperature at SWVP. The dotted lines show the concentrations of $H_4GeO_4^0$ and $H_3GeO_4^-$ in equilibrium with GeO_2(tet) at each temperature, and the heavy curves represent the total solubility. Based on the data of Pokrovski and Schott (1998).

Table 22
Summary of solubility products of $In(OH)_3(s)$ from the literature

Medium	Temperature (°C)	log K_{s0}	Source
?	?	−33	25H
0?	25?	−33.9	49L
0	25	−36.9	59AS
0	20	−32.9	61K
0	25	−36.9	86BM
0	25	−39.8	91K

Sources: 25H—Heyrovský (1925); 49L—Lacroix (1949); 59AS—Aksel'rud and Spivakovskii (1959); 61K—Kovalenko (1961); 86BM—Baes and Mesmer (1986); 91K—Kochetkova et al. (1991).

In mobility in the presence of reduced sulfur should be quite restricted, barring the presence of ligands stronger and/or more abundant than bisulfide or hydroxide.

In order to determine the effect of chloride on the solubility of $In_2S_3(s)$, In–chloride and –hydroxychloride complexes were added to the solubility model described above. Thus, the total solubility expression given above was modified by adding $InCl^+$, $InCl^{2+}$, $InCl_3^0$, $InCl_4^-$ and $InOHCl^+$. The stability constants for these complexes at 1-M ionic strength were calculated from the parameters given by Baes and Mesmer (1986). The results are shown in Fig. 25, from which it can be seen that the chloride complexes contribute significantly to the solubility of $In_2S_3(s)$ only at pH <3. Thus, at least at low temperatures, the solubility of $In_2S_3(s)$ is quite low even in the presence of significant amounts of chloride. However, given the lack of data available, it is impossible to predict how the solubility would change with increasing temperature or pressure.

Table 23
Summary of solubility products of $In_2S_3(s)$ from the literature

Medium	Temperature (°C)	log K_{s0}	Source
0	25	−73.24	62TS
1 M $NaClO_4$	20	−77.4	70TS
0	25	−96.3	88L

Sources: 62TS—Terpilowski and Staroscik (1962); 70TS—Tunaboylu and Schwarzenbach (1970); 88L—Licht (1988).

A solubility product (log K = −21.63) has been reported for $InPO_4(s)$ by Deichman et al. (1968). However, we have encountered no reports of the occurrence of such a phase as a mineral. The solubility product for $InPO_4(s)$ is similar in magnitude to that for $GaPO_4(s)$, so we may conclude that $InPO_4(s)$ also is probably too soluble to precipitate under most geologically reasonable conditions.

5.5. Scandium

With the exception of $ScPO_4(s)$, solubility products for most of the primary scandium minerals listed in the Introduction are generally not available. In this section we discuss the solubility of the oxyhydroxide ScOOH as a means of placing some limits on the probable concentrations of Sc in aqueous solutions under various conditions. As with the other cases considered in this study, more stable Sc phases would be expected to be less soluble. There seems to be some disagreement as to whether the formula of the Sc oxyhydroxide phase is ScOOH(s) (Schindler,

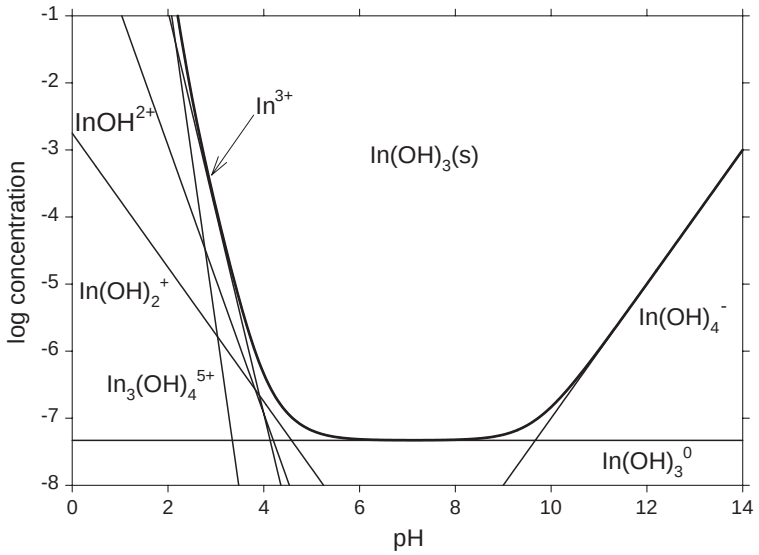

Fig. 23. Solubility of $In(OH)_3(s)$ vs. pH at 25 °C and zero ionic strength. The light lines show the concentrations of individual In(III) species in equilibrium with $In(OH)_3(s)$ and the heavy curve represents the total solubility. See text for discussion of data sources.

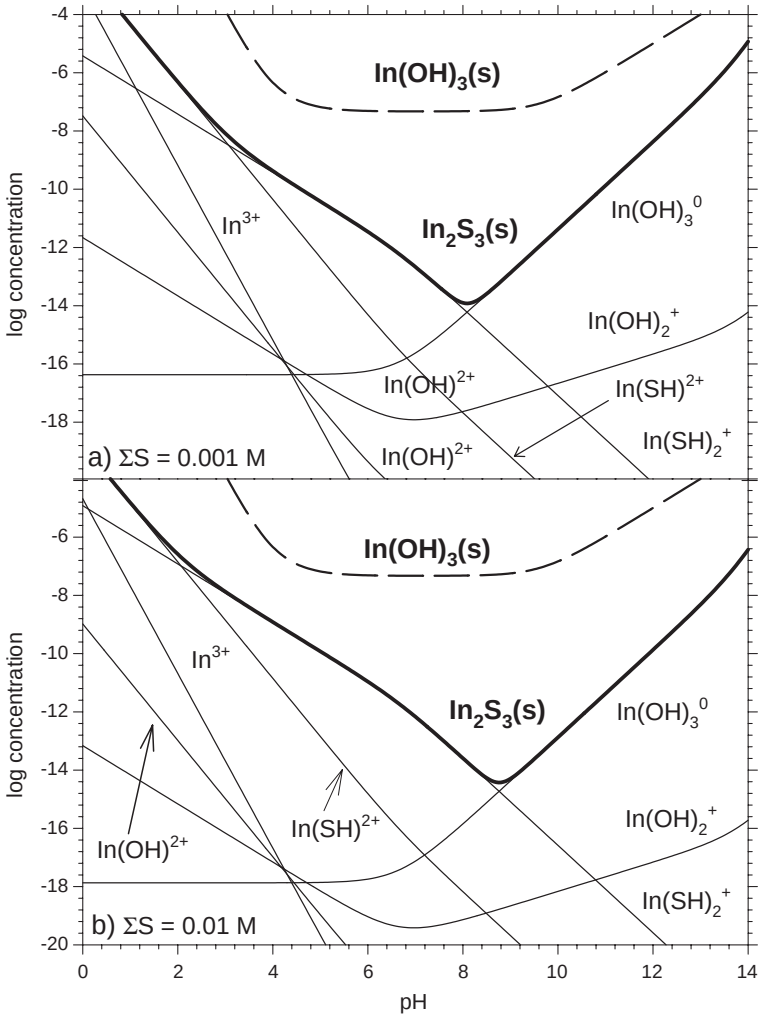

Fig. 24. Solubility of In_2S_3(s) as a function of pH and total dissolved sulfide at 20 °C and 1 M $NaClO_4$ (based on the data of Tunaboylu and Schwarzenbach, 1970). The light lines show the concentrations of In^{3+}, and In–bisulfide and In–hydroxide complexes in equilibrium with In_2S_3(s) and the heavy curve represents the total solubility. The diagrams are drawn for total dissolved sulfide values of: (a) 0.001 M; and (b) 0.01 M. The dotted line shows the solubility of $In(OH)_3$(s) from Fig. 23 for reference.

1963; Baes and Mesmer, 1986) or $Sc(OH)_3$(s) (Aksel'rud, 1963; Feitknecht and Schindler, 1963), but the measured solubility products are similar, irrespective of the formula assumed (Table 24). We adopt the solubility product recommended by Baes and Mesmer (1986) for ScOOH(s) to calculate the solubility diagram depicted in Fig. 26. The figure shows that ScOOH(s) has a moderately broad solubility minimum of $10^{-6.7}$ M (~9 ppb) which extends from pH ~6 to pH ~10. Below pH 6, the solubility increases dramatically with decreasing pH, attaining a value of approximately 10^{-2} M (490 ppm) at pH =4. Thus, at low temperatures in the absence of components that might form more stable Sc phases, it appears that substantial Sc could be transported at moderately acidic conditions even in the absence of strong ligands. The solubility of ScOOH(s) in pure water at 25 °C and slightly acidic to near-neutral pH is higher that that of either GaOOH(s) or $In(OH)_3$(s). Above pH =10, the solubility of ScOOH(s) is predicted also to increase due to the formation of the anionic $Sc(OH)_4^-$ species, but this increase will not generally be of significance in nature.

Limited data are available for the solubility of scandium orthophosphate [$ScPO_4$], which occurs in nature as the mineral pretulite and in hydrated form as kolbeckite [$ScPO_4 \cdot 2H_2O$]. The equilibrium constant of the reaction

$$ScPO_4(S) \leftrightarrow Sc^{3+} + PO_4^{3-} \quad (26)$$

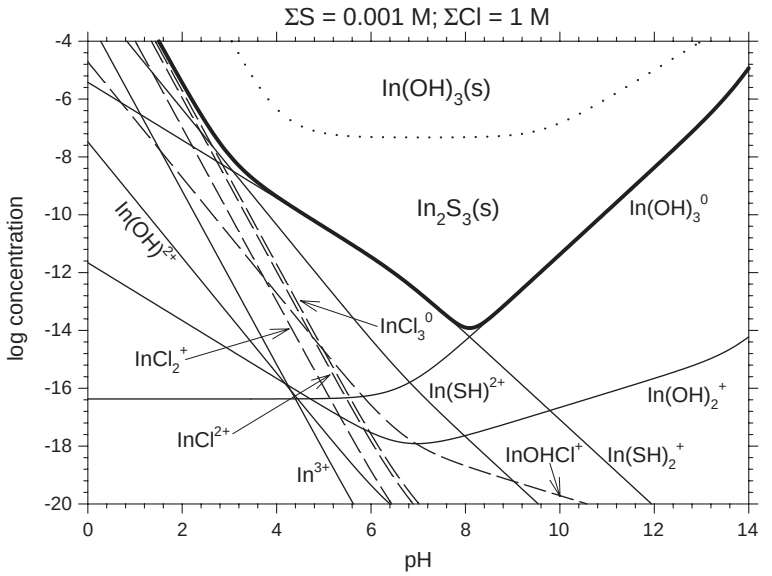

Fig. 25. Solubility of In_2S_3(s) as a function of pH at 20 °C, 1 M total chloride, and 0.001 M total sulfide. The light solid lines show the concentrations of In^{3+}, and In–bisulfide, and In–hydroxide complexes in equilibrium with In_2S_3(s) and the heavy curve represents the total solubility. The light dashed lines show the concentrations of the In–chloride and In–hydroxychloride complexes in equilibrium with In_2S_3(s). The dotted line shows the solubility of $In(OH)_3$(s) from Fig. 23 for reference.

is given as log $K_{s0}=-26.96$ by Yaglov et al. (1974). From the solubility data of Komissarova et al. (1971b) a value of log $K_{s0}=-26.0$ can be estimated. We have calculated the solubility of $ScPO_4$(s) as a function of pH at 25 °C and $\Sigma PO_4=10^{-5}$ mol, assuming that only hydroxide complexes and the phosphate complex $Sc(H_2PO_4)^{2+}$ are present; the results are shown in Fig. 27. For this calculation, we have adopted log $K_{s0}=-26.96$ from Yaglov et al. (1974), the hydrolysis constants of Sc^{3+} recommended by Baes and Mesmer (1986) (see also Table 18), and log $\beta_1=4.72$ for $Sc(H_2PO_4)^{2+}$ from Laskorin et al. (1970). If $Sc(H_2PO_4)^{2+}$ is the only significant Sc–phosphate complex and the stability constant of Laskorin et al. (1970) is correct, then Sc–phosphate complexes do not appear to contribute significantly more to $ScPO_4$(s) solubility than Sc^{3+} and the various hydroxide species (Fig. 27). However, other Sc–phosphate complexes may well be important. Fig. 27 suggests that Sc mobility will be reduced in the presence of phosphate owing to the lower solubility of $ScPO_4$(s) compared to $Sc(OH)_3$(s) at pH <9. At pH >9, it appears that the phosphate is more soluble (less stable) than the hydroxide, but such pH values would be rarely encountered in most geological environments. Although increasing temperature could change the situation, we tentatively conclude that simultaneous transport of large quantities of Sc and phosphate in the same solution is unlikely.

Table 24
Summary of solubility products of ScOOH(s) and $Sc(OH)_3$(s) from the literature

Solid	Medium	Temperature (°C)	log K_{s0}	Source
ScOOH	1 M $NaClO_4$	25	−30.8	63S
ScOOH	0	25	−32.6	86BM
$Sc(OH)_3$	0	25	−29.7	61A
$Sc(OH)_3$	0	25	−33	63FS
$Sc(OH)_3$	0	20	−29.1 to −29	63KB
$Sc(OH)_3$	0	25	−29.7	63A

Sources: 61A—Aksel'rud (1961); 63S—Schindler (1963); 63FS—Feitknecht and Schindler (1963); 63KB—Kovalenko and Bagdasarov (1963); 63A—Aksel'rud (1963); 86BM—Baes and Mesmer (1986).

6. Conclusions

In this study we have reviewed critically the available thermodynamic data relevant to the aqueous mass transfer of Ga, Ge, In and Sc in ore-forming environments. From an examination of these data we can draw the following conclusions:

1) The most common oxidation states of these metals in aqueous solution are Ga(III), Ge(IV), In(III), and Sc(III).
2) Owing to their high charge, the hydrated ions of these metals are Pearson hard-acids, meaning they prefer to form complexes with hard ligands such as hydroxide, fluoride, sulfate and phosphate. However,

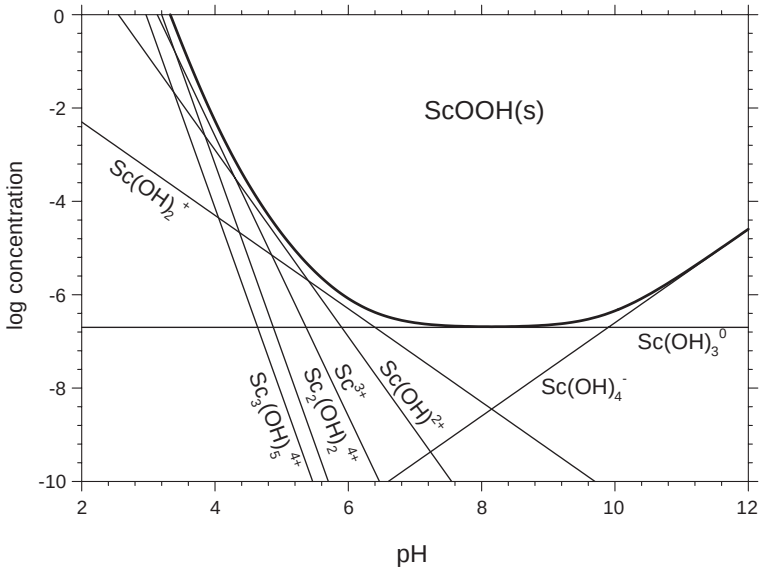

Fig. 26. Solubility of ScOOH(s) as a function of pH at zero ionic strength and 25 °C. The light lines show the concentrations of individual Sc(III) species in equilibrium with ScOOH(s) and the heavy curve represents the total solubility. See text for discussion of data sources.

In(III) is markedly softer than the other three, and exhibits a greater tendency to form complexes with chloride and bisulfide.

3) The hydrated Ga^{3+}, In^{3+} and Sc^{3+} ions exhibit octahedral coordination, and it is expected that their complexes with small ligand numbers also have this same coordination. However, there is evidence, in the case of In and Ga, that as the ligand number approaches four at elevated temperatures, the complex takes on a tetrahedral geometry.
4) Data on these metals in geothermal fluids and other natural waters suggests that their concentrations will be in the sub-ppm range (and generally in the sub-ppb range) in common hydrothermal fluids.
5) There is a general lack of reliable data on stability constants for relevant metal complexes at elevated

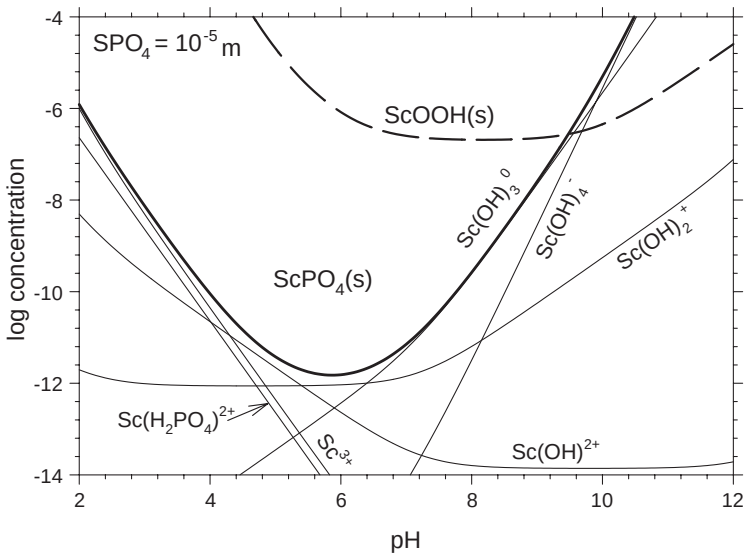

Fig. 27. Solubility of $ScPO_4$(s) as a function of pH at a total phosphate concentration of 10^{-5} M, zero ionic strength and 25 °C. The light lines show the concentrations of individual Sc(III) species in equilibrium with $ScPO_4$(s) and the heavy curve represents the total solubility. The dashed curve shows the solubility of ScOOH(s) for comparison. See text for discussion of data sources.

temperature, and in many cases data are absent or highly uncertain even under standard conditions. However, the data appear sufficiently reliable to propose recommended values at 25 °C, 1 bar and infinite dilution for the following: hydroxide complexes of all four metals, fluoride complexes of Ga, In and Sc, chloride complexes of In, and sulfate complexes of Ga, In and Sc.

6) On the basis of the available stability constant data, we predict that hydroxide and fluoride complexes are the most likely forms of transport of Ga and Sc, germanic acid is the most likely form of transport of Ge, and hydroxide, fluoride, chloride and bisulfide complexes may be important, depending on conditions, in the transport of In.
7) Solubility products of relevant solid phases containing these metals are generally not available. However, solubility products of the following phases have been reported: α-GaOOH(s), $GaPO_4$(s), $In(OH)_3$(s), In_2S_3(s), $InPO_4$, GeO_2(hex), GeO_2(tet), ScOOH(s), and $ScPO_4$(s). Data are available for α-GaOOH(s), GeO_2(hex), and GeO_2(tet) at elevated temperatures. These data provide at least some constraints on the maximum concentrations of Ga, Ge, In and Sc to be expected in aqueous fluids at geologically reasonable conditions.
8) Low solubilities of α-GaOOH(s) in the absence of fluoride or strong organic ligands at low temperatures are consistent with the known immobility of Ga during weathering processes and the accumulation of this metal to economic levels in some bauxites.
9) Experimental studies of the complexation and solubility of Ga, Ge, In and Sc, especially at elevated temperatures and pressures, is a fruitful area for future research.

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References

Ahrland, S., 1967. Enthalpy and entropy changes by formation of different types of complexes. Helvetica Chimica Acta 50, 306–318.

Akalin, S., Özer, U.Y., 1971. Hydrolysis of Sc^{3+}_{aq} and the stabilities of scandium(III)-tiron chelates in aqueous solution. Journal of Inorganic and Nuclear Chemistry 33, 4171–4180.

Akitt, J.W., Gessner, W., 1984. Aluminum-27 nuclear magnetic resonance investigation of highly alkaline aluminate solutions. Journal of the Chemical Society. Dalton Transactions, 147–148.

Aksel'rud, N.V., 1961. Basic chlorides and hydroxides of scandium. Ukrainskii Khimicheskii Zhurnal 27, 431–437 (in Russian).

Aksel'rud, N.V., 1963. Basic chlorides and hydroxides of elements of the scandium and lanthanide subgroups. Uspekhi Khimii 32, 800–822 (in Russian).

Aksel'rud, N.V., Spivakovskii, V.B., 1959. Basic chlorides and hydroxides of indium. Russian Journal of Inorganic Chemistry 4, 449–453.

Alekseeva, I.I., Nemzer, I.I., 1971. State of germanium(IV) in acid solutions. Russian Journal of Inorganic Chemistry 16, 987–989.

Alimarin, I.P., Belyavskaya, T.A., Brikina, G.D., 1965. Investigation of the complex formation of scandium by the ion exchange method. Vestnik Moskovskogo Universiteta. Seria 2, Himia 5, 69–72.

Altynov, V.I., Ptitsyn, B.V., 1962. Theory of the silver chloride electrode and determination of the instability constants of complex chlorides. Russian Journal of Inorganic Chemistry 7, 1088–1091.

Andrianov, A.M., Nazarenko, V.A., 1966. Hydroxo-complexes of germanium(IV). Russian Journal of Inorganic Chemistry 11, 816–819.

Antikainen, P.J., 1957. Ionization and some thermodynamic properties of germanic acid in aqueous solutions. Suomen Kemistilehti 30B, 123–128.

Antikainen, P.J., 1960. Studies on concentrated oxyacid solutions prepared by ion exchange: I. Equilibria involving mono- and polynuclear oxyacids of germanium. Suomen Kemistilehti 33B, 38–40.

Antonovich, V.P., Nazarenko, V.A., 1968. Spectrophotometric determination of the hydrolysis constants of scandium ions. Russian Journal of Inorganic Chemistry 13, 940–941.

Arnórsson, S., 1984. Germanium in Icelandic geothermal systems. Geochimica et Cosmochimica Acta 48, 2489–2502.

Aveston, J., 1966. Hydrolysis of scandium(III): ultracentrifugation and acidity measurements. Journal of the Chemical Society. A. Inorganic, Physical, Theoretical, 1599–1601.

Aziz, A., Lyle, S.J., 1968. Partition studies of chemical equilibria in indium(III) fluoride and sulphate systems. Journal of Inorganic and Nuclear Chemistry 30, 3223–3229.

Aziz, A., Lyle, S.J., 1969a. A study of the hydrolysis of indium and lanthanum ions by partition methods. Journal of Inorganic and Nuclear Chemistry 31, 2431–2435.

Aziz, A., Lyle, S.J., 1969b. Equilibrium constants for aqueous fluoro complexes of scandium, yttrium, americium(III) and curium(III) by extraction into di-2-ethylhexyl phosphoric acid. Journal of Inorganic and Nuclear Chemistry 31, 3471–3480.

Baes Jr., C.F., Mesmer, R.E., 1986. The Hydrolysis of Cations. Krieger Publishing Company, Malabar, Florida. 489 pp.

Belyavskaya, T.A., Alimarin, I.P., Brykina, G.D., 1966. An ion exchange study of complex formation by scandium. Vestnik Moskovskogo Universiteta. Seria 2, Himia 21, 84–87.

Bénézeth, P., Diakonov, I.I., Pokrovski, G.S., Dandurand, J.-L., Schott, J., Khodakovsky, I.L., 1997. Gallium speciation in aqueous solution. Experimental study and modelling: Part 2. Solubility of α-GaOOH in acidic solutions from 150 to 250 °C and hydrolysis constants of gallium(III) to 300 °C. Geochimica et Cosmochimica Acta 61, 1345–1357.

Benoit, R.L., Clerc, P., 1961. Chlorogermanium(IV) species in acid media. Journal of Physical Chemistry 65, 676–680.

Benoit, R.L., Place, J., 1963. Fluoride complexes of germanium(IV) in aqueous solutions. Canadian Journal of Chemistry 41, 1170–1180.

Bereslavtseva, L.F., Toropova, T.G., 1959. On the solubility of indium hydroxide. Izvestiya Vysshikh Uchebnykh Zavedenii Khimiya i Khimicheskaya Tekhnologiya 2, 97–100 (in Russian).

Bernhard, F., Walter, F., Ettinger, K., Taucher, J., Mereiter, K., 1998. Pretulite, $ScPO_4$, a new scandium mineral from the Styrian and Lower Austrian lazulite occurrences, Austria. American Mineralogist 83, 625–630.

Bernstein, L.R., Waychunas, G.A., 1987. Germanium crystal chemistry in hematite and goethite from the Apex Mine, Utah, and some new data on germanium in aqueous solution and in stottite. Geochimica et Cosmochimica Acta 51, 623–630.

Biedermann, G., 1956. Studies on the hydrolysis of metal ions: Part 14. The hydrolysis of the indium(III) ion: In^{3+}. Arkiv för Kemi 9, 278–293.

Biedermann, G., Ferri, D., 1982. On the polynuclear hydrolysis of the indium ion: In^{3+}. Acta Chemica Scandinavica A36, 611–622.

Biedermann, G., Kilpatrick, M., Pokras, L., Sillén, L.G., 1956. Studies on the hydrolysis of metal ions. 18. The scandium ion, Sc^{3+}. Acta Chemica Scandinavica 10, 1327–1339.

Biedermann, G., Li, N.C., Yu, J., 1961. Studies on the hydrolysis of metal ions: Part 34. The hydrolysis of the indium(III) ion, In^{3+}, in 3 M $(Na^{+})Cl^{-}$ medium. Acta Chemica Scandinavica, 555–564.

Biryuk, E.A., Nazarenko, V.A., 1973. Determination of the hydrolysis constants of monomeric gallium ions in solutions with ionic strength 0.1–1.0. Russian Journal of Inorganic Chemistry 18, 1576–1578.

Biryuk, E.A., Nazarenko, V.A., Ravitskaya, R.V., 1969. Spectrophotometric determination of the hydrolysis constants of indium ions. Russian Journal of Inorganic Chemistry 14, 503–506.

Botelho, N.F., Roger, G., d'Yvoire, F., Moëlo, Y., Volfinger, M., 1994. Yanomamite, $InAsO_4 \cdot 2H_2O$, a new indium mineral from topaz-bearing greisen in the Goias tin province, Brazil. European Journal of Mineralogy 6, 245–254.

Bottazzini, N., Crespi, V., Perini, F., 1973. Le costanti di associazione in soluzione acquosa dei sistemi: H–F, Cu^{II}–Fe In^{III}–F, valutate con l'elettrodo selettivo per lo ione fluoruro. La Chimica e L'Industria (Milan), vol. 55, pp. 697–701.

Brown, P.L., 1989. The hydrolysis of metal ions: Part 11. The ionic strength dependence of gallium (III). Journal of the Chemical Society. Dalton Transactions, 399–402.

Brown, P.L., Ellis, J., Sylva, R.N., 1982. The hydrolysis of metal ions: Part 4. Indium(III). Journal of the Chemical Society. Dalton Transactions, 1911–1914.

Brown, P.L., Ellis, J., Sylva, R.N., 1983. The hydrolysis of metal ions: Part 6. Scandium(III). Journal of the Chemical Society. Dalton Transactions, 35–36.

Burton, J.D., Culkin, F., 1978. Gallium. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry II-3. Springer-Verlag, Berlin, pp. 32-D-7.

Busaev, A.I., Kanaev, N.A., 1959. Computation of the stability constant of some complex compounds of indium by the method of uniform variations using data obtained with the aid of cationite. Vestnik Moskovskogo Universiteta, Seriya Matematiki, Mekhaniki, Astronomii, Fiziki, Khimii 14, 135–143 (in Russian).

Busey, R.H., Mesmer, R.E., 1977. Ionization equilibria of silicic acid and polysilicate formation in aqueous sodium chloride solutions to 300 °C. Inorganic Chemistry 16, 2444–2450.

Caminiti, R., Paschina, G., 1981. An X-ray diffraction study of the structure of the aqua indium(III) ion in indium sulfate solution. Chemical Physics Letters 82, 487–491.

Campisi, A., Tregloan, P.A., 1985. Kinetics and equilibria of Ga(III)–thiocyanate complex formation. Mechanism of ligand substitution reactions of Ga (III) in aqueous solution. Inorganica Chimica Acta 100, 251–259.

Cantinolle, P., Laforet, C., Maurel, C., Picot, P., Grangeon, J., 1985. Contribution á la mineralogie de l'indium; decouverte en France de deux nouveaux sulfures d'indium et de deux nouvelles occurrences de roquesite. Bulletin de Mineralogie 108, 245–248.

Carleson, B.G.F., Irving, H., 1954. The stability constants of the indium halides. Journal of the Chemical Society, 4390–4399.

Carpéni, G., 1948. Équilibres électrolytiques entre ions, molécules simples et molécules condensées.—II. Le point "isohydrique". Conséquences et applications. Bulletin de la Societe Chimique de France 15, 629–637.

Ciavatta, L., Iuliano, M., Porto, R., Vasca, E., 1990. Fluorogermanate(IV) equilibria in acid media. Polyhedron 9, 1263–1270.

Cozzi, D., Vivarelli, S., 1953. Beitrag zur Chemie des Indiums. Zeitschrift für Elektrochemie 57, 408–416.

Cozzi, D., Vivarelli, S., 1954. Beitrag zur Chemie des Indiums. II. Zeitschrift für Elektrochemie 58, 907–912.

Crerar, D.A., Wood, S.A., Brantley, S.L., Bocarsly, A.B., 1985. Chemical controls on solubility of ore-forming minerals in hydrothermal solutions. Canadian Mineralogist 23, 333–352.

Criaud, A., Fouillac, C., 1986. Étude des eaux thermominérales carbogazeuses du Massif Central Français: II. Comportement de quelques métaux en trace, de l'arsenic, de l'antimoine et du germanium. Geochimica et Cosmochimica Acta 50, 1573–1582.

Davydov, Yu.P., Glazacheva, G.I., 1980. Hydrolysis of the scandium(III) ion in aqueous solutions. Russian Journal of Inorganic Chemistry 25, 1462–1467.

Deichman, E.N., Rodicheva, G.V., Krysina, L.S., 1966. Reaction of indium sulphate with sodium sulphate in aqueous solution. Russian Journal of Inorganic Chemistry 11, 1199–1201.

Deichman, E.N., Tananaev, I.V., Ezhova, Zh.A., Kuz'mina, T.N., 1968. Indium phosphate. Russian Journal of Inorganic Chemistry 13, 23–25.

De la Cuadra, A., 1990. On polygermanate ion (review and critical study). Anales de Quimica 86, 221–229.

Diakonov, I.I., Pokrovski, G.S., Bénézeth, P., Schott, J., Dandurand, J.-L., Escalier, J., 1997. Gallium speciation in aqueous solution. Experimental study and modelling: Part 1. Thermodynamic properties of $Ga(OH)_4^-$ to 300 °C. Geochimica et Cosmochimica Acta 61, 1333–1343.

Duma, T.W., Marsicano, F., Hancock, R.D., 1991. The affinity of gallium(III) and indium(III) for nitrogen donor ligands. Journal of Coordination Chemistry 23, 221–232.

Dutrizac, J.E., Jambor, J.L., Chen, T.T., 1986. Host minerals for the gallium–germanium ores of the Apex Mine, Utah. Economic Geology 81, 946–950.

Evdokimov, D.Ya., Kogan, E.A., 1963. A study of germanium dioxide solubility in water at different temperatures. Ukrainskii Khimicheskii Zhurnal 29, 1020–1022 (in Russian).

Faktor, M.M., Carasso, J.I., 1965. Tetragonal germanium dioxide and equilibria in the Ge–O–H system. Journal of the Electrochemical Society 112, 817–822.

Feitknecht, W., Schindler, P., 1963. Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure and Applied Chemistry 6, 129–199.

Ferri, D., 1972a. On the complex equilibria between indium(III) and chloride ions. Acta Chemica Scandinavica 26, 733–746.

Ferri, D., 1972b. On the hydrolysis of the indium(III) ion in chloride solutions. Acta Chemica Scandinavica 26, 747–759.

Ferri, D., Salvatore, F., Vasca, E., Miranda, R., 1994. Complex formation equilibria at high ligand concentration: Indium(III)–chloride complexes. Annali di Chimica 84, 141–149.

Fetter, N.R., 1957. The equilibria of crystalline gallium oxide monohydrate in dilute solutions of perchloric acid and sodium hydroxide at 25 °C. Ph.D. thesis, University of Oregon (University Microfilms Publ. No. 20195).

Fiat, D., Connick, R.E., 1966. Magnetic resonance studies of ion solvation. Co-ordination number of gallium(III) ions in aqueous solutions. Journal of the American Chemical Society 80, 4754.

Filatova, L.N., 1980. Determination of the stability of the indium(III) orthophosphato-complexes. Russian Journal of Inorganic Chemistry 25, 1474–1475.

Filatova, L.N., Galochkina, G.V., 1974. Study of orthophosphate complexes of Group III elements by the ion exchange method. Soviet Radiochemistry 16, 591–596.

Filatova, L.N., Kurdyumova, T.N., 1974. Study of complex formation of indium with orthophosphoric acid. Russian Journal of Inorganic Chemistry 19, 1746–1747.

Fridman, Ya.D., Sorochan, R.I., Dolgashova, N.V., 1962. Stability of thallium mixed halides and of indium mixed halides in solution. Russian Journal of Inorganic Chemistry 7, 1100–1104.

Gammons, C.H., Wood, S.A., Williams-Jones, A.E., 1996. The aqueous geochemistry of the rare earth elements and yttrium: VI. Stability of neodymium chloride complexes at 25 °C to 300 °C. Geochimica et Cosmochimica Acta 60, 4615–4630.

Gamsjäger, H., Schindler, P., 1967. Löslichkeitsprodukte von Metalloxiden und -hydroxiden. 11. Die Löslichkeit von α-GaO(OH) bei 60°C in perchlorsäuren Lösungen konstanter Ionenstärke. Helvetica Chimica Acta 50, 2053–2057.

Gayer, K.H., Zajicek, O.T., 1964. The solubility of germanium(IV) oxide in aqueous NaOH solutions at 25 °C. Journal of Inorganic and Nuclear Chemistry 26, 951–954.

Geldron, A., 1983. Le germanium: un élément valorisant des gisements hydrothermaux à Zn–Cu–(Pb). Chronique de la Recherche Minière 470, 25–32.

Gimblett, F.G.R., 1971. Particle growth and precipitation in hydrolyzed gallium(IIII) perchlorate solutions. Journal of Inorganic and Nuclear Chemistry 33, 2887–2903.

Goguel, R., 1988. Ultratrace metal analysis of New Zealand geothermal waters by ICP-MS. Trace Elements in New Zealand: Environmental, Human and Animal, Proceedings, New Zealand Trace Elements Group Conference, 30 November–2 December 1988. Lincoln College, Canterbury, pp. 263–270.

Gordienko, V.I., 1974. pH-potentiometric determination of the composition of hydroxo complexes and of the hydrolysis constants of salts of weak bases at high ionic strengths: II. Products of first stage of hydrolysis. Journal of General Chemistry of the USSR 44, 853–859.

Grammaccioli, C.M., Diella, V., Demartin, F., 1999. The role of fluoride complexes in REE geochemistry and the importance of 4f electrons: some examples in minerals. European Journal of Mineralogy 11, 983–992.

Grammaccioli, C.M., Diella, V., Demartin, F., 2000. The formation of scandium minerals as an example of the role of complexes in the geochemistry of rare earths and HFS elements. European Journal of Mineralogy 12, 795–808.

Gulezian, C.E., Müller, J.H., 1932. The conductivity and degree of hydrolysis of sodium bigermanate and the primary dissociation constant of germanic acid. Journal of the American Chemical Society 54, 3151–3158.

Haas, J., Konopik, N., Mark, F., Neckel, A., 1964a. Zur polymerisation der Germaniumsäure, 1. Mitt. Bestimmung der mittleren Ladungszahlen und mittleren Polymerisationsgerade auf Grund potentiometrischer Titrationen. Monatshefte für Chemie 95, 1141–1165.

Haas, J., Konopik, N., Mark, F., Neckel, A., 1964b. Zur polymerisation der Germaniumsäure, 2. Ermittlung der Komplexzusammensetzungen und Berechnung der Stabilitätskonstanten auf Grund graphischer Ausgleichsverfahren. Monatshefte für Chemie 95, 1166–1172.

Haas, J., Konopik, N., Mark, F., Neckel, A., 1964c. Zur polymerisation der Germaniumsäure, 3. Ermittlung der Komplexzusammensetzungen und der Stabilitätskonstanten mehrkerniger Komplexe auf Grund rechnerischer Ausgleichsverfahren. Monatshefte für Chemie 95, 1173–1187.

Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare earth elements in hydrothermal systems: estimates of standard partial molal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. Geochimica et Cosmochimica Acta 59, 4329–4350.

Häkkinen, P., Purokoski, S., Lajunen, K., 1986. A potentiometric study on the complex formation of germanic acid and germanate ion with sugar acids and disaccharides in aqueous solution. Finnish Chemical Letters 13, 93–97.

Haladjian, J., Carpéni, G., 1967. Recherches sur le point isohydrique et les phénomènes de condensation ou d'association (XXIV) — Étude életrométrique de l'isopolycondensation du cation hydraté $[Ga,aq]^{3+}$, à 25 °C, en milieu KCl (c_{Cl^-}=3 M). Journal de Chimie Physique et de Physico-Chimie Biologique 64, 1338–1344.

Hamid, Sh.A., Alimarin, I.P., Puzdrenkova, I.V., 1965. Determination of the hydrolysis constant and the complex formation constant of In^{3+} with n-benzoylphenylhydroxylamine by the extraction method. Vestnik Moskovskogo Universiteta, Ser. 2, Khimiya 3, 71–75 (in Russian).

Hancock, R.D., Marsicano, F., Rudolph, E., 1980. The fluoride complexes of the trivalent first-row metal ions, with special reference to the fluoride complexes of V(III) and Sc(III). Journal of Coordination Chemistry 10, 223–227.

Hanson, M.P., Plane, R.A., 1969. Raman spectroscopic study of stepwise bromide and chloride complexes of indium(III) in aqueous solution. Inorganic Chemistry 8, 746–750.

Hasegawa, Y., 1970. The behaviour of indium(III) complexes in several liquid–liquid distribution system: I. A solvent extraction study of indium(III) complexes in aqueous perchlorate media containing several anionic ligands. Bulletin of the Chemical Society of Japan 43, 2665–2670.

Hasegawa, Y., Shimada, T., Nitsu, M., 1980. Solvent extraction of 3B group metal ions from hydrochloric acid with trioctylphosphine oxide. Journal of Inorganic and Nuclear Chemistry 42, 1487–1489.

Hattox, E.M., de Vries, T., 1936. The thermodynamics of aqueous indium sulfate solutions. Journal of the American Chemical Society 58, 2126–2129.

Helgeson, H.C., Kirkham, D.H., Flowers, G.C., 1981. Theoretical predictions of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. calculation of activity coefficients, osmotic coefficients and apparent molal and standard and relative partial molar properties to 600 °C and 5 kbar. American Journal of Science 281, 1249–1516.

Hemmes, P., Rich, L.D., Cole, D.L., Eyring, E.M., 1970. Kinetics of the hydrolysis of aqueous indium(III) and gallium(III) perchlorates. Journal of Physical Chemistry 74, 2859–2862.

Henderson, P., 1982. Inorganic Geochemistry. Pergamon Press, New York. 353 pp.

Hepler, L.G., Hugus Jr., Z.Z., 1952. Hydrolysis and halide complexing of indium(III). Journal of the American Chemical Society 74, 6115–6116.

Hepler, L.G., Kury, J.W., Hugus Jr., Z.Z., 1954. Complexing of indium(III) by fluoride ions in aqueous solution: free energies, heats and entropies. Journal of Physical Chemistry 58, 26–28.

Heyrovský, J., 1925. Contribution to the analytical chemistry of indium. Chemicke Listy 19, 168–172 (in Czech).

Hörmann, P.K., 1978. Germanium B-M. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry II-3. Springer-Verlag, Berlin, p. 31-D-10.

Ingri, N., 1963. Equilibrium studies of polyanions. 12. Polygermanates in Na(Cl) medium. Acta Chemica Scandinavica 17, 597–616.

Ingri, N., Schorsch, G., 1963. On the determination of formation constants of $Ge_2(OH)_2^{2-}$ using a hydrogen-electrode. Measurements in 3 M Na(Cl)-medium. Acta Chemica Scandinavica 17, 590–596.

Ivanov-Emin, B.N., Nisel'son, L.A., Ivolgina, A.T., 1960. The solubility of scandium hydroxide in caustic soda solutions. Russian Journal of Inorganic Chemistry 5, 1372–1373.

Ivanov-Emin, B.N., Nisel'son, L.A., Gvozdera, N.I., 1962. Solubility of gallium hydroxide in sodium hydroxide and potassium hydroxide solutions at 25°. Russian Journal of Inorganic Chemistry 7, 591–592.

Ivanov-Emin, B.N., Borzova, L.D., Zaitsev, B.E., Mekes Fisher, M., 1968. Solubility of scandium hydroxide in potassium hydroxide solutions. Russian Journal of Inorganic Chemistry 13, 1156–1157.

Ivanov-Emin, B.N., Susanin, T.N., Egorov, A.M., Ryzhikov, V.P., Zaitsev, B.E., Ezhov, A.I., 1976. Monofluoro-pentaaquoscandium chloride. Soviet Journal of Coordination Chemistry 2, 687–690.

Izatt, R.M., Eatough, D., Christensen, J.J., Bartholomew, C.H., 1969. Calorimetrically determined log K, ΔH°, and ΔS° values for the interaction of sulphate ion with several bi- and ter-valent metal ions. Journal of the Chemical Society. A. Inorganic, Physical, Theoretical, 47–53.

Jablonski, Z., Jablonski, H., 1978. Complexes of gallium(III): Part II. Study of the system: gallium triperchlorate–sodium fluoride–water. Prace Naukowe Politechniki Szczecinskiej 90, 43–50 (in Polish).

Jander, G., Pluskal, H., 1957. Untersuchungen über die Hydrolyse von Gallium(III)-und Indium(III)-salzen in wässriger Lösung und über Gallatlösungen. Zeitschrift für Anorganische und Allgemeine Chemie 291, 67–75.

Jarv, T., Bulmer, J.T., Irish, D.E., 1977. An investigation of the digitized Raman band profiles of aqueous indium(III) chloride solutions. Journal of Physical Chemistry 81, 649–656.

Johan, Z., Oudin, E., Picot, P., 1983. Analogues germaniféres et galliféres des silicates et oxydes dans les gisements de zinc de Pyrenées centrales, France: argutite et carboirite, deux nouvelles espèces minérales. Tschermaks Mineralogische und Petrologische Mitteilungen 31, 97–119.

Kalidas, C., Knoche, W., Papadopoulos, D., 1971. On the mechanism of ligand substitution in weak complexes III. Berichte der Bunsen-Gesellschaft Physical Chemistry Chemical Physics 75, 106–110.

Kawakami, H., Koga, A., Nozaki, H., 1956. Distribution of As and Ge in the Beppu Thermal Springs, Japan. Journal of the Chemical Society of Japan (Pure Chemistry Section) 77, 1785–1789.

Kilpatrick, M., Pokras, L., 1953. The acid dissociation of the aquoscandium ions. Journal of the Electrochemical Society 100, 85–92.

Kilpatrick, M., Pokras, L., 1954. The acid dissociation of the aquoscandium ions: II. The effect of temperature and of ionic strength. Journal of the Electrochemical Society 101, 39–43.

Kleiner, K.E., 1960. Calculation of the stability or solubility of complex compounds in coloured solutions from spectrophotometric data. Russian Journal of Physical Chemistry 34, 194–197.

Kleiner, K.E., Gridchina, G.I., 1960. Fluoride complexes of gallium(III) in aqueous solutions. Russian Journal of Inorganic Chemistry 5, 96–99.

Kochetkova, G.M., Toptygina, G.M., Soklakova, O.V., Evdokimov, V.I., 1991. The reaction of indium trichloride with calcium carbonate in aqueous solution. Russian Journal of Inorganic Chemistry 36, 944–947.

Koga, A., 1967. Germanium, molybdenum, copper and zinc in New Zealand thermal waters. New Zealand Journal of Science 10, 428–446.

Komissarova, L.N., Prutkova, N.M., Pushkina, G.Ya., 1971. Stability of hydroxo-ions of scandium in aqueous solution. Russian Journal of Inorganic Chemistry 16, 954–956.

Komissarova, L.N., Mel'nikov, P.P., Teterin, E.G., Chuvaev, V.F., 1971. Scandium phosphates. Russian Journal of Inorganic Chemistry 16, 1414–1416.

Kondziela, P., Biernat, J., 1975. Determination of stability constants of indium halogenide complexes by polarography. Electroanalytical Chemistry and Interfacial Electrochemistry 61, 281–288.

Kosova, T.B., Dem'yanets, L.N., 1988. Behaviour of germanium dioxide in water and aqueous solutions at temperatures of 25–300 °C. Russian Journal of Inorganic Chemistry 33, 1522–1527.

Kosova, T.B., Dem'yanets, L.N., Uvarova, T.G., 1987. Investigation of the solubility of germanium dioxide in water at 25–300 °C. Russian Journal of Inorganic Chemistry 32, 430–432.

Kovalenko, P.N., 1961. Polarographic determination of the solubility of indium hydroxide. Russian Journal of Inorganic Chemistry 6, 275–277.

Kovalenko, P.N., Bagdasarov, K.N., 1963. Determination of the pH of initial dissolution and precipitation of scandium hydroxide using photocolorimetry. Izvestiya Vysshikh Uchebnykh Zavedenii Khimiya i Khimicheskaya Tekhnologiya, 546–552 (in Russian).

Kraus, K.A., Nelson, F., Smith, G.W., 1954. Anion-exchange studies: IX. Adsorbability of a number of metals in hydrochloric acid solutions. Journal of Physical Chemistry 58, 11–17.

Kraynov, S.R., 1965. Geochemistry of fluorine, tungsten, and germanium in nitrogenous thermal waters of crystalline rocks. Geochemistry International 2, 1001–1011.

Kraynov, S.R., 1967. Geochemistry of germanium in the thermal carbonate waters (illustrated by examples from the Pamirs and the Greater Caucasus). Geochemistry International 4, 309–320.

Krüger, G., Thilo, E., 1958. Über das hydrolytische Verhalten und die Molekulargewichte von Germanat-und Stannationen in schmelzendem Glaubersalz. Zeitschrift für Physikalische Chemie (Leipzig) 209, 190–205.

Krupp, R.E., Seward, T.M., 1987. The Rotokawa geothermal system, New Zealand: an active epithermal gold-depositing environment. Economic Geology 82, 1109–1129.

Kul'ba, F.Ya., Yakovlev, Yu.B., Zenchenko, D.A., 1974. Hydrolysis of indium(III) ions in mixed aqueous dimethyl sulphoxide and

aqueous dimethylformamide solutions. Russian Journal of Inorganic Chemistry 19, 502–504.

Kul'ba, F.Ya., Yakovlev, Yu.B., Zenchenko, D.A., 1975a. Potentiometric investigation of the hydrolysis of indium(III) ions in water–acetonitrile solutions. Russian Journal of Inorganic Chemistry 20, 994–998.

Kul'ba, F.Ya., Zenchenko, D.A., Yakovlev, Yu.B., 1975b. Hydrolysis of indium(III) ions in mixed water–acetone solutions. Russian Journal of Inorganic Chemistry 20, 1314–1315.

Kury, J.W., Paul, A.D., Hepler, L.G., Connick, R.E., 1959. The fluoride complexing of scandium(III) in aqueous solution: free energies, heats and entropies. Journal of the American Chemical Society 81, 4185–4189.

Lacroix, S., 1949. Étude de quelques complexes et composés peu solubles des ions Al^{3+},Ga^{3+}, In^{3+}. Annales Chimie (Paris) 4, 5–83.

Laubengayer, A.W., Morton, D.S., 1932. Germanium: XXXIX. The polymorphism of germanium dioxide. Journal of the American Chemical Society 54, 2303–2320.

Laskorin, B.N., Smirnov, V.F., Nikonov, V.I., 1970. Complex formation by scandium in phosphoric acid solutions. Russian Journal of Inorganic Chemistry 15, 1724–1726.

Lasztity, S., 1977. Determination of the hydrolysis constants of indium(III) ions by liquid ion exchange and tracer indication. Radiochemical and Radioanalytical Letters 29, 215–222.

Licht, S., 1988. Aqueous solubilities, solubility products and standard oxidation–reduction potentials of the metal sulfides. Journal of the Electrochemical Society 135, 2971–2973.

Liferovich, R., Gogol, O., 1999. Genesis of Sc-bearing mineral associations of Kovdor Massif according to Sr isotope data. Journal of Conference Abstracts 4, 296.

Lindqvist-Reis, P., Muñoz-Páez, A., Díaz-Moreno, S., Pattanaik, S., Persson, I., Sandström, M., 1998. The structure of the hydrated gallium(III), indium(III), and chromium(III) ions in aqueous solution. A large angle X-ray scattering and EXAFS study. Inorganic Chemistry 37, 6675–6683.

Linn Jr., T.A., Schmitt, R.A., 1974. Indium. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry II-4. Springer-Verlag, Berlin, p. 49-D-1-4.

Lourijsen-Teyssèdre, M., 1955. Contributions à l'étude des phénomènes de condensation en chimie minérale. 10. Constitution des solutions de germanates et d'arsénites. Bulletin de la Societé Chimique de France 22, 1118–1125.

Lundeen, M., Hugus, Z.Z., 1992. A calorimetric study of some metal ion complexing equilibria. Thermochimica Acta 196, 93–103.

Maeda, M., Ohtaki, O., 1977. An X-ray diffraction study on the structure of the aqua indium(III) ion in perchlorate solution. Bulletin of the Chemical Society of Japan 50, 1893–1894.

Martell, A.E., Smith, R.M., 1998. NIST critically selected stability constants of metal complexes. Reference Database 46, version 5.0. National Institute of Standards and Technology. Gaithersburg, Maryland.

Meisser, N., Thelin, P., Chiappero, P.-J., Maurel, C., 1999. Laforetite, $AgInS_2$, a new mineral of the chalcopyrite group from the Montogros Mine, Haute-Loire, France. European Journal of Mineralogy 11, 891–897.

Mikešová, M., Bartušek, M., 1979. Complexes of germanic acid with mannitol, sorbitol, maltol, and with chromotropic and kojic acids. Collection Czechoslovak Chemical Communications 44, 3256–3263.

Mikhailova, D.M., Nacheva, R.N., Mikhailova, V.Ts., 1969. Stability constants of chloride complexes of indium in the presence of alkali metal nitrates as the base electrolyte. Soviet Radiochemistry 11, 241–245.

Mikhailyuk, Yu.I., Gordienko, V.I., 1974. Composition and instability constants of the simplest fluoro-complexes of gallium(III). Russian Journal of Inorganic Chemistry 19, 114–115.

Mikhailyuk, Yu.I., Gordienko, V.I., 1975. Composition and instability constants of the simplest phosphato-complexes of gallium(III). Russian Journal of Inorganic Chemistry 20, 241–245.

Moeller, T., 1941. Contributions to the chemistry of indium: II. The hydrolysis of indium trichloride solutions. Journal of the American Chemical Society 63, 1206–1207.

Moeller, T., King, G.L., 1950. Some physicochemical studies on gallium(III) salt solutions. Journal of Physical Chemistry 54, 999–1011.

Morris, D.F.C., Andrews, B.D., 1967. The stability of halide complexes of gallium. Electrochimica Acta 12, 41–48.

Mortlock, R.A., Froelich, P.N., Feely, R.A., Massoth, G.J., Butterfield, D.A., Lupton, J.E., 1993. Silica and germanium in Pacific Ocean hydrothermal vents and plumes. Earth and Planetary Science Letters 119, 365–378.

Motchany, A.I., Chvanski, P.P., Leonyuk, N.I., 2000. Synthesis and solubility of $GaPO_4$ crystals in acid solutions under hydrothermal conditions. Journal of Crystal Growth 211, 506–508.

Müller, J.H., 1926. Further studies on the allotrophy of germanium oxide. Proceedings American Philosophical Society, vol. 65, pp. 183–195.

Muñoz-Páez, A., Díaz-Moreno, S., Sánchez Marcos, E., Martínez, J.M., Pappalardo, R.R., Persson, I., Sandström, M., Pattanaik, S., Lindqvist-Reis, P., 1997. EXAFS study of the hydration structure of Ga^{3+} aqueous solution. Journal de Physique IV 7 (C2), 647–648.

Nanda, R.K., Aditya, S., 1962. Studies on ions association equilibria. Spectrophotometric determination of the thermodynamic instability constants of $AlSO_4^+$, $GaSO_4^+$, and $InSO_4^+$. Zeitschrift für Physikalische Chemie, Neue Folge 35, 139–145.

Nazarenko, V.A., Flyantikova, G.V., 1968. Cationic hydroxo-complexes of germanium(IV) in solutions with ionic strength 0–1. Russian Journal of Inorganic Chemistry 13, 966–969.

Nazarenko, V.A., Flyantikova, G.V., Lebedeva, N.V., 1962. On the ionic composition of germanium in weakly acidic solutions. Ukrainskii Khimicheskii Zhurnal 28, 66–67 (in Russian).

Nazarenko, V.A., Antonovich, V.P., Nevskaya, E.M., 1968. Spectrophotometric determination of the hydrolysis constants of gallium ions. Russian Journal of Inorganic Chemistry 13, 825–828.

Nishida, H., 1976. Spectrophotometric study of the gallium and Chromazurol S (1:2) complex. Bunseki Kagaku 25, 866–868 (in Japanese).

Nozaki, Y., Lerche, D., Alibo, D.S., Tsutsumi, M., 2000a. Dissolved indium and rare earth elements in three Japanese rivers and Tokyo Bay: evidence for anthropogenic Gd and In. Geochimica et Cosmochimica Acta 64, 3975–3982.

Nozaki, Y., Lerche, D., Alibo, D.S., Snidvongs, A., 2000b. The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. Geochimica et Cosmochimica Acta 64, 3983–3994.

Ottemann, J., Nuber, B., 1972. Brunogeierit, ein Germanium-Ferritspinell von Tsumeb. Neues Jahrbuch für Mineralogie, 263–267.

Palmer, D.A., Wesolowski, D.J., 1992. Aluminum speciation and equilibria in aqueous solution: II. The solubility of gibbsite in acidic sodium chloride solutions from 30 to 70 °C. Geochimica et Cosmochimica Acta 56, 1065–1091.

Parpiev, N.A., Maslennikov, I.A., 1968. Investigation of fluoride complexes of silicon and germanium by the ion exchange method. Uzbekskii Khimicheskoi Zhurnal 2, 6–9 (in Russian).

Paul, A., 1962. The chloride and bromide complexing of scandium(III) and yttrium(III) in aqueous solution. Journal of Physical Chemistry 66, 1248–1252.

Pearson, R.G., 1963. Hard and soft acids and bases. Journal of the American Chemical Society 85, 3533–3539.

Pentcheva, E., 1964. Sur le critère microchimique charactérisant les eaux thermales azotées de Bulgarie. Comptes Rendus de al Académie Bulgare des Sciences 17, 1021–1024.

Pokrovski, G.S., Diakonov, I.I., Bénézeth, P., Gurevich, V.M., Gavrichev, K.S., Gorbunov, V.E., Dandurand, J.-L., Schott, J., Khodakovsky, I.L., 1997. Thermodynamic properties of gallium hydroxide oxide (α-GaOOH) at temperatures to 700 K. European Journal of Mineralogy 9, 941–951.

Pokrovski, G.S., Schott, J., 1998. Thermodynamic properties of aqueous Ge(IV) hydroxide complexes from 25 to 350 °C: implications for behavior of germanium and the Ge/Si ratio in hydrothermal fluids. Geochimica et Cosmochimica Acta 62, 1631–1642.

Pugh, W., 1929. Germanium: Part V. The hydrolysis of sodium germanate and the dissociation constants of germanic acid. Journal of the Chemical Society, 1994–2001.

Raade, G., Ferraris, G., Gula, A., Ivaldi, G., Bernard, F., 2002. Kristiansenite, a new calcium-scandium-tin sorosilicate from granite pegmatite in Tordal, Telemark, Norway. Mineralogy and Petrology 75, 89–99.

Reed, G.L., Sutton, K.J., Morris, D.F.C., 1964. Stability constants of scandium(III) chloride complexes. Journal of Inorganic and Nuclear Chemistry 26, 1227–1231.

Riley, J.P., 1961. Composition of mineral water from the hot spring at Bath. Journal of Applied Chemistry (London) 11, 190.

Rossotti, F.J.C., Rossotti, H., 1956. Studies on the hydrolysis of metal ions: XV. Partition equilibria in the system ^{114}In/TTA/benzene. Acta Chemica Scandinavica 10, 779–792.

Roth, W.A., Schwartz, O., 1926. Physikalisch-chemische Eigenschaften der Lösungen von Germaniumdioxyd (und Arsentrioxyd). Chemische Berichte 59, 338–348.

Rudolph, W.W., Pye, C.C., 2000. Raman spectroscopic measurements of scandium(III) hydration in aqueous perchlorate solution and ab initio molecular orbital studies of scandium(III) water clusters: does Sc(III) occur as a hexaaqua complex? Journal of Physical Chemistry A 104, 1627–1639.

Ruff, J.K., Tyree, S.Y., 1958. Light scattering studies on aqueous gallium perchlorate solutions. Journal of the American Chemical Society 80, 5654–5657.

Ryhl, T., 1969. Thermodynamic properties of indium(III) halogenide and thiocyanate complexes in aqueous solution. Acta Chemica Scandinavica 23, 2667–2676.

Ryss, I.G., Kulish, N.F., 1964a. Equilibrium of the first hydrolysis stage of the hexafluorogermanate ion. Russian Journal of Inorganic Chemistry 9, 603–607.

Ryss, I.G., Kulish, N.F., 1964b. Hydrolysis of potassium hexafluorogermanate in aqueous solution. Russian Journal of Inorganic Chemistry 9, 752–754.

Ryss, I.G., Kulish, N.F., 1965. Overall equilibrium constant for hydrolysis of the hexafluorogermanate ion GeF_6^{2-} at 25°. Russian Journal of Inorganic Chemistry 10, 996–1000.

Sakanoue, M., 1960. Geochemical studies on the radioactive sediments: IV. Uranium and germanium in the carbonaceous materials found in the "Misasa group" sedimentary beds of the Tertiary. Nippon Kagaku Zasshi 81, 1520–1523.

Samodelov, A.P., 1964. State and complex formation of scandium in solutions of mineral acids. Soviet Radiochemistry 6, 548–560.

Schindler, P., 1963. Die Bestimmung der Löslichkeitskonstanten von Metalloxiden und -hydroxiden. Chimia (Switzerland) 17, 313–330.

Schischkova, L.G., 1974. Untersuchung der Komplexbilduing von Gallium(III) mit Ammoniumsulfat und Bestimmung der Stabilitätskonstante des erhaltenen Komplexes nach der Ionenaustauschmethode. Comptes Rendus de la Académie Bulgare des Sciences 27, 1545–1548.

Schlyter, K., 1961. Thermochemical studies on the hydrolysis of the Indium(III) ion. Transactions of the Royal Institute of Technology Stockholm, Sweden 182, 3–41.

Schufle, J.A., Eiland, H.M., 1954. Indium halide complexes studied by ion-exchange methods. Journal of the American Chemical Society 76, 960–962.

Schufle, J.A., Stubbs, M.F., Witman, R.E., 1951. A study of indium(III) chloride complexes by polarographic methods. Journal of the American Chemical Society 73, 1013–1015.

Schwarz, R., Huf, E., 1931. Beiträge zur Chemie des Germaniums: VIII. Mitteilung. Über das Germaniumdioxyd. Zeitschift für anorganisch Une Allgemeine Chemie 203, 188–218.

Schwarz-Schampera, U., Herzig, P.M., 1997. Geochemistry of In in VMS deposits: implications from active hydrothermal vents in the Southern Lau Basin (SW-Pacific). In: Papunen, H. (Ed.), Mineral Deposits: Research and Exploration, Where Do They Meet? A.A. Balkema, Rotterdam, pp. 379–382.

Schweitzer, G.K., Winkley, D.C., 1967. The first hydrolysis constant of the scandium(III) ion measured by a solvent extraction technique. In: Dyrssen, D., Liljenzin, J.O., Rydberg, J. (Eds.), Solvent Extraction Chemistry. Proceedings, International Conference, Gothenburg, Sweden, 1966. North-Holland Publ. Co., Amsterdam, pp. 39–45.

Sekine, T., Hasegawa, Y., 1966. Studies of scandium in various solutions: I. An ion-exchange study of scandium(III) chloride and nitrate complexes. Bulletin of the Chemical Society of Japan 39, 240–243.

Sekine, T., Hasegawa, Y., 1977. Solvent Extraction Chemistry. Marcel Dekker, New York, p. 273.

Seward, T.M., Henderson, C.M.B., Charnock, J.M., 2000. Indium(III) chloride complexing and solvation in hydrothermal solutions to 350 °C: an EXAFS study. Chemical Geology 167, 117–127.

Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A (Foundations) 32, 751–767.

Shock, E.L., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high temperatures and pressures: correlation algorithms for ionic species and equation fo state predictions to 5 kbar and 1000 °C. Geochimica et Cosmochimica Acta 52, 2009–2036.

Shock, E.L., Sassani, D.C., Willis, M., Sverjensky, D.A., 1997. Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. Geochimica et Cosmochimica Acta 61, 907–950.

Sohrin, Y., 1991. Formation of halide complexes of methyl- and inorganic germanium(IV) in aqueous hydrohalogenic acid solutions. Bulletin of the Chemical Society of Japan 64, 3363–3371.

Sokolovskaya, L.V., Polyvyannyi, I.R., 1980. Study of the solubility, viscosity, and electrical conductivity in the system $NaInS_2$–Na_2S–H_2O. Academia Nauk Kazhakhskoi SSR, Institut Metallurgi i Obogashchemia, No. 3899 (VINITI Deposited Document), 12 pp. (in Russian).

Stryapkov, A.V., Koshei, E.V., Stryapkova, R.Zh., 1996. Hydrolytic precipitation of scandium from nitrate, chloride and sulfate solutions. Izvestiya Ministerstva Nauki-Akademii Nauk Respubliki Kazakhstan Seriya Khimicheskaya 4, 60–65 (in Russian).

Sundén, N., 1954a. On the complex chemistry of the indium ion: Part III. The iodide, thiocyanate, and fluoride systems. Svensk Kemisk Tidskrift 66, 50–61.

Sundén, N., 1954b. On the complex chemistry of the indium ion: Part II. The chloride, bromide, and sulfate systems. Svensk Kemisk Tidskrift 66, 20–33.

Sundén, N., 1954c. On the complex chemistry of the indium ion: Part IV. An investigation of the chloride and sulfate systems by ion exchangers. Svensk Kemisk Tidskrift 66, 173–178.

Sundén, N., 1954d. On the complex chemistry of the indium ion: Part V. The chloride, bromide, and sulfate systems from extraction equilibria. Svensk Kemisk Tidskrift 66, 345–350.

Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000 °C and 5 kb. Geochimica et Cosmochimica Acta 61, 1359–1412.

Swift, T.J., Fritz Jr., O.G., Stephenson, T.A., 1967. Determination of the hydration number of gallium(III) in aqueous solution. Journal of Chemical Physics 46, 406.

Tananaev, I.V., Chudinova, N.N., 1964. Preparation and properties of normal gallium phosphate. Russian Journal of Inorganic Chemistry 9, 135–138.

Tanger, J.C., Helgeson, H.C., 1988. Revised equation of state for the standard partial molal properties of ions and electrolytes. American Journal of Science 288, 19–98.

Tateda, A., 1965. The cation exchange investigation of scandium acetate and sulfate systems. Bulletin of the Chemical Society of Japan 38, 165–171.

Terpilowski, J., Staroscik, R., 1962. On solubility of In_2S_3. Chemia Analityczna 7, 629–633.

Tóth, I., Zékány, L., Brücher, E., 1984. Equilibrium study of the systems of aluminium(III), gallium(III) and indium(III) with mercaptoacetate, 3-mercaptopropionate and 2-mercaptobenzoate. Polyhedron 3, 871–877.

Tóth, I., Zékány, L., Brücher, E., 1985. Comparative study of hydroxo-fluoro and hydroxo-sulphido mixed ligand complexes of aluminium(III) and gallium(III). Polyhedron 4, 279–283.

Travers, J.G., Dellien, I., Helper, L.G., 1976. Scandium: thermodynamic properties, chemical equilibria, and standard potentials. Thermochimica Acta 15, 89–104.

Tuck, D.G., 1983. Critical evaluation of equilibrium constants in solution: Part A. Stability constants of metal complexes. Critical survey of stability constants of complexes of indium. Pure and Applied Chemistry 55, 1477–1528.

Tunaboylu, K., Schwarzenbach, G., 1970. Die Löslichkeit von Indiumsulfid. Chimia (Switzerland) 24, 424–427.

Turner, D.R., Whitfield, M., Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25 °C and 1 atm pressure. Geochimica et Cosmochimica Acta 45, 855–881.

Tur'yan, Ya.I., Strizhov, N.K., 1972. Polarographic determination of the instability constant of the sulphato-complex of indium(III). Russian Journal of Inorganic Chemistry 17, 1066–1067.

Tur'yan, Ya.I., Tikhanov, I.A., Strizhov, N.K., 1982. Electroreduction of In(III) ions catalyzed by halide and thiocyanate ions, and the polarographic determination of the stability constants of halide and thiocyanate complexes of indium. Russian Journal of General Chemistry 52, 1520–1525.

Uchida, M., Okuwaki, A., 1997. Solubility of gallium(III) hydroxide in aqueous NaCl solutions at 100 °C. Journal of Solution Chemistry 26, 699–708.

Uchida, M., Okuwaki, A., 1998. Potentiometric determination of the first hydrolysis constant of gallium(III) in NaCl solution to 100 °C. Journal of Solution Chemistry 27, 965–978.

Usherenko, L.N., Skorik, N.A., 1972. Hydrolysis of rare earth metal, yttrium, scandium, and thorium ions in water and in water–ethanol mixtures. Russian Journal of Inorganic Chemistry 17, 1533–1535.

Uzumasa, Y., Nasu, Y., 1960. Chemical investigations of hot springs in Japan: LVII. Gallium in hotsprings. Nippon Kagaku Zasshi 81, 732.

Uzumasa, Y., Nasu, Y., Toshiko, S., 1959. Chemical investigations of hot springs in Japan: XLIX. Germanium contents of hot springs. Nippon Kagaku Zasshi 80, 1118–1128.

Vagramjan, A.T., Leshawa, T.I., 1967. Untersuchung der Potentiale von Galliumelektroden und der Polarisation beim elektrolytischen Abscheiden von Gallium in Abhängigkeit von dessen Aggregatzustand. Zeitschrift für Physikalische Chemie (Leipzig) 234, 57–70.

van Gaans, P.F.M., van Miltenburg, J.C., 1991. Thermodynamics of aqueous gallium chloride. Heats of solution and dilution at 25 °C. Journal of Solution Chemistry 20, 335–360.

van Gaans, P.F.M., Oonk, H.A.J., Somsen, G., 1990. Thermodynamics of aqueous gallium chloride. Apparent molar volumes and heat capacities at 25 °C. Journal of Solution Chemistry 19, 831–854.

Vavra, S., Rudenko, N.P., 1964. Sorption of indium on Kationite KU-2 and stability constants of indium chloride complexes in water–ethanol solutions. Vestnik Moskovskogo Universiteta, Ser. 2, Khimiya 6, 14–17 (in Russian).

Vasil'ev, V.P., Kozlovskii, E.V., 1974. Thermodynamics of the reactions for the formation of indium(III) fluoro-complexes in aqueous solution. Russian Journal of Inorganic Chemistry 19, 807–809.

Vehov, V.A., Birtuhnovskaya, B.S., Doronkina, R.F., 1964. Changes of germanium dioxide solubility in water from 0 to 100 °C. Izvestiya Vysshikh Uchebnykh Zavedenii Khimiya i Khimicheskaya Tekhnologiya 7, 1018–1019 (in Russian).

Walker, J.B., Twine, C.R., Choppin, G.R., 1971. Thermodynamic parameters of fluoride complexes of Group IIIA ions. Journal of Inorganic and Nuclear Chemistry 33, 1813–1817.

Wang, N., 1978. New data for Ag_8SnS_6 (canfieldite) and Ag_8GeS_6 (argyrodite). Neues Jahrbuch für Mineralogie Monatsheft, 269–272.

Weissberg, B.G., Browne, P.R.L., Seward, T.M., 1979. Ore metals in active geothermal systems. In: Barnes, H.L. (Ed.), Geochemistry of Hydrothermal Ore Deposits, 2nd edition. John-Wiley and Sons, New York, pp. 738–780.

Wesolowski, D.J., 1992. Aluminum speciation and equilibria in aqueous solution: I. The solubility of gibbsite in the system Na–K–Cl–OH–$Al(OH)_4$ from 0 to 100 °C. Geochimica et Cosmochimica Acta 56, 1065–1091.

White, J.M., Kelly, P., Li, N.C., 1961. Dinonyl naphthalene sulphonic acid and tri-n-octylamine as liquid ion-exchangers for the study of Fe(III) and In(III)–chloride complexes. Journal of Inorganic and Nuclear Chemistry 16, 337–344.

Wilson, A.S., Taube, H., 1952. The affinities of chromic ion and gallium ion for fluoride. Journal of the American Chemical Society 74, 3509–3512.

Wood, S.A., 1990. The aqueous geochemistry of the rare earth elements and yttrium: Part I. Review of available low temperature

data for inorganic complexes and the inorganic REE speciation of natural waters. Chemical Geology 82, 159–186.

Wood, S.A., 1992. Theoretical prediction of speciation and solubility of beryllium in hydrothermal solution to 300 °C at saturated vapor pressure: application to bertrandite/phenakite deposits. Ore Geology Reviews 7, 249–278.

Wood, S.A., Samson, I.M., 1998. Solubility of ore minerals and complexation of ore metals in hydrothermal solutions. In: Richards, J., Larson, P. (Eds.), Techniques in Hydrothermal Ore Deposits. Reviews in Economic Geology, vol. 10, pp. 33–80.

Wood, S.A., Palmer, D.A., Wesolowski, D.J., Bénézeth, P., 2002. The aqueous geochemistry of the rare earth elements and yttrium: Part XI. The solubility of $Nd(OH)_3$ and hydrolysis of Nd^{3+} from 30 to 290 °C at saturated water vapor pressure with in-situ pH_m measurement. In: Hellmann, R., Wood, S.A. (Eds.), Water–Rock Interaction, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar. Geochemical Society Special Publication, vol. 7, pp. 229–256.

Woodward, L.A., Nord, A.A., 1956. Raman spectrum of tetrachlorogallate ion ($GaCl_4^-$) in aqueous solution. Journal of the Chemical Society, 3721–3722.

Woodward, L.A., Taylor, M.J., 1960. Raman effect and solvent extraction: Part II. Spectra of the tetrachloroindate and tetrachloroferrate ions. Journal of the Chemical Society, 4473–4477.

Yakovlev, Yu.B., Ravlenko, L.I., 1980. Hydrolytic equilibria for the indium(III) ion in aqueous acetonitrile solutions. Russian Journal of Inorganic Chemistry 25, 673–675.

Yakovlev, Yu.B., Ravlenko, L.I., 1981. Hydrolytic equilibria of the indium(III) ion in water–dioxan solutions. Russian Journal of Inorganic Chemistry 26, 1424–1426.

Yaglov, V.N., Novikov, G.I., Sharap, L.A., Lefarova, K.Kh., Marinova, L.A., 1974. Heat of formation of scandium orthophosphate. Russian Journal of Physical Chemistry 48, 446.

Yakovlev, Yu.B., Ravlenko, L.I., Barsukova, O.V., 1981. Hydrolytic equilibria for indium(III) in aqueous dimethyl sulphoxide solutions. Russian Journal of Inorganic Chemistry 26, 817–820.

Yuchi, A., Hotta, H., Wada, H., Nakagawa, G., 1987. Mixed ligand complexes of trivalent metal ions with an amine-N-polycarboxylate and fluoride. Bulletin of the Chemical Society of Japan 60, 1379–1382.

Zelyanskaya, A.I., Bausova, N.V., Kukalo, L.Ya., 1958. Polarographic properties of gallium and indium. Trudy Institut Metallurgi, Academia Nauk SSSR, Ural Filial 2, 263–274 (in Russian).