The aqueous solution thermodynamics of niobium under conditions of environmental and biological interest

Filella, Montserrat; May, Peter M.

How to cite

FILELLA, Montserrat, MAY, Peter M. The aqueous solution thermodynamics of niobium under conditions of environmental and biological interest. In: Applied Geochemistry, 2020, vol. 122, n° 104729, p. 1–9. doi: 10.1016/j.apgeochem.2020.104729

This publication URL: https://archive-ouverte.unige.ch/unige:143471
Publication DOI: 10.1016/j.apgeochem.2020.104729

Applied Geochemistry 122 (2020) 104729

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: http://www.elsevier.com/locate/apgeochem

The aqueous solution thermodynamics of niobium under conditions of environmental and biological interest

Montserrat Filella [a,*], Peter M. May [b]

[a] Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205, Geneva, Switzerland
[b] College of Science, Health, Engineering and Education, Murdoch University, Murdoch, WA, 6150, Australia

ARTICLE INFO

Editorial handling by Prof. M. Kersten

Keywords:
Niobium
Equilibrium constants
Solubility

ABSTRACT

The available equilibrium constant data for reactions of niobium in aqueous solution have been critically evaluated and entered into a thermodynamic database. The relevant literature is sparse and, where comparable, often inconsistent. Problems include poor characterisation of solid phases and limitations with older analytical techniques. Nevertheless, the JESS suite of computer programs has been applied where possible to achieve thermodynamic consistency and provide a critically-selected set of equilibrium constants that could be useful for modelling purposes. However, the utility of the resulting set is evidently limited by a lack of adequate data. This is unfortunate given the significance of niobium in radioactive waste management and certain catalytic applications.

1. Introduction

Niobium is a naturally occurring chemical element which belongs to Group 5 of the Periodic Table. It has oxidation states ranging from –I to + VII but under all redox conditions found in biological and environmental systems only Nb(V) exists. Since Nb(V) has a high charge and a relatively small ionic radius, niobium behaves as a strong Pearson's hard metal, favouring binding by hard donors such as oxygen-containing ligands and fluoride.

The solution chemistry of niobium has received some attention from the radioactive waste community because of isotopes such as: ^{91}Nb (half-life: 68 y), ^{93m}Nb (half-life of 16.3 y), a fission product, and ^{94}Nb (half-life of 20×10^3 y), a neutron activation isotope formed in nuclear power plants. Although the element does not pose particular environmental problems except those directly related to its production (Schulz et al., 2017; Paquet et al., 2019), it is now receiving increased attention because of its status as a 'technology-critical element' (Gunn, 2014).

We seek here to establish a working thermodynamic description of niobium in aqueous, multicomponent media involving its most important interactions with relevant low-molecular-mass (l.m.m.) ligands. Our aim is to develop a predictive tool that will help future investigations of the environmental chemistry and (eco)toxicology of this element requiring a coherent thermodynamic database.

2. Methodology

The first step in this review of niobium thermodynamics has been to collect as much equilibrium constant data from the chemical literature as possible. The IUPAC Stability Constants Database (http://www.acadsoft.co.uk/scdbase/scdbase.htm) has been used as the starting point of a systematic 'up-tree' citation search strategy. This has been supplemented with other sources as necessary. Niobium has been the object of several critical compilations mostly due to its relevance to radioactive waste management (Lothenbach et al., 1999; Wood, 2004; Kitamura et al., 2010).

Computer-assisted harmonisation of thermodynamic parameters of chemical reactions to achieve overall consistency is now well established (May and Rowland, 2018). Sets of reliable standard Gibbs energies of reaction and their corresponding equilibrium constants are readily determined from all reaction data accumulated beforehand from the literature. The procedure involves an ordered Gaussian elimination to determine the so-called 'basis species' together with the linear combinations of reactions that are used to describe the whole chemical system. The ordering of the reactions depends on 'weights' assigned during compilation to each datum for the conditional equilibrium constants, $log_{10}K^{\circ}$, and reaction enthalpies, ΔH°, at given temperature and ionic strength. Estimates of the relevant standard thermodynamic quantities (*i.e.*, at 1 bar and infinite dilution), at 25 °C, are determined

* Corresponding author.
E-mail addresses: montserrat.filella@unige.ch (M. Filella), P.May@murdoch.edu.au (P.M. May).

https://doi.org/10.1016/j.apgeochem.2020.104729
Received 7 June 2020; Received in revised form 26 July 2020; Accepted 6 August 2020
Available online 15 August 2020

by least squares regression using a well-established function (May, 2000) based on the IUPAC-recommended SIT equation to express, where possible, the effects of activity coefficient change. The way this works in practice is illustrated by example in the Supplementary Information. Results are not accompanied by any objective function because values are, in general, normalised so have they no absolute value other than in the minimisation process.

3. Results

All relevant species for which equilibrium constants have been found have been included in the database; the published associated equilibrium constant values are given in Tables 1–3 in the form expressed by their authors. Results are shown in Tables 5 and 6 for infinite dilution (0 mol/L ionic strength). Constant values are not accompanied by confidence intervals, which can only be based on the propagation of random errors, in circumstances where systematic errors are overwhelmingly dominant. Users of the data need to assess for themselves the impact of these systematic errors on their model calculation. Auxiliary data needed for a number of reactions have been taken from JESS database (http://jess.murdoch.edu.au).

3.1. Niobium acid-base chemistry and oxide solubility

Published solubility values are shown in Fig. 1, experimental conditions in solubility experiments appear in Table 4, and published equilibrium constants are summarised in Table 1. At first sight, the solubility data appear even more scattered than usual, despite allowing for variations due to different conditions (i.e., temperature and ionic strength).

The oldest study is by Babko et al. (1963). They found an extended isoelectric range (from pH 0 to 7) and measured elemental niobium's solubility in this range to be 1.4×10^{-5} mol L^{-1}. This solubility value was later assigned by Baes and Mesmer (1976) to estimate the log of the solubility product of $Nb_2O_5(s)$ (-5.2 for $1/2\ Nb_2O_5(s) + 5/2\ H_2O = Nb(OH)_5$) and also used by Etxebarria et al. (1994) (-10.71 for $Nb_2O_5(s) + 5\ H_2O = 2\ Nb(OH)_5$). The precipitate was prepared *in situ* and its composition and structure were not determined.

Yajima et al. (1992) and Yajima (1994) studied the same system some 30 years later. Their publications are not now available but have been captured in detail in the compilations by Lothenbach et al. (1999) and Kitamura et al. (2010). Yajima and co-workers measured solubilities both from over- and undersaturation from 7 to 28 days. Lothenbach et al. (1999) and Kitamura et al. (2010) calculated solubility products from the original data.

Pfeiffer et al. (2010) performed an extensive and careful study at different ionic strengths and temperatures based on undersaturation experiments with B–$Nb_2O_5(s)$. Later, Timofeev et al. (2015) measured solubility for niobium from commercial $Nb_2O_5(s)$ at 150 and 250 °C in mildly acidic conditions (log solubility product of -11.23 for $Nb_2O_5(s) + 2\ H^+ + 3\ H_2O = 2\ Nb(OH)_4^+$ at 150 °C). They observed a tendency of $Nb_2O_5(s)$ solubility to increase slightly over the temperature range from 150 to 250 °C.

The large difference in measured solubility values can be ascribed to different solid phases having been formed but it also unveils a doubtful dependence of solubility values on the detection limit of the technique used to measure 'dissolved' niobium (Table 4). Babko et al. (1963), reported on a "freshly precipitated niobium hydroxide" but "(probably) amorphous compounds" were also studied by Yajima and co-workers who found considerably different solubilities, associated with differences in detection limits. Sensible comparisons are largely precluded since Babko's precipitate was not otherwise characterised and Lothenbach et al. (1999) give no additional detail. Interestingly, Kitamura et al. (2009) suggested that Yajima's XRD detection limits might have been a key limiting factor so these results should thus be regarded as "at least" values.

Peiffert et al. (2010) studied monoclinic B–$Nb_2O_5(s)$ and Timofeev et al. (2017) a non-characterised commercially-available $Nb_2O_5(s)$. Niobium pentoxide exists in many polymorphic forms (Fig. 2). According to Schäfer et al. (1966), the polymorphs are classified based on the temperature at which they are obtained starting from amorphous niobium oxide, passing through the following crystalline phases: T (orthorhombic) and TT (pseudohexagonal or monoclinic) which crystallize at lower-temperatures (~700–900 K), B (monoclinic) and M (tetragonal) at medium-temperature (~900–1200 K), and H (monoclinic) at high-temperature (1223 K). First-principle calculations of the properties of the T and B phases showed that B–Nb_2O_5 has lower concentration of acid sites compared to T-Nb_2O_5 (Pinto et al., 2017). Since most studies in the area are motivated by the use of niobium oxide in technological applications such as catalysis, the modification due to ageing of the amorphous phase, which is the most relevant in the context of environmental and biochemical media, remains largely unexplored.

Babko et al. (1963) also calculated pK values for $Nb(OH)_5$ in solution. These pK values have been cited by Baes and Mesmer (1976) and other compilations (e.g., Byrne, 2002). Values on the acidic zone were obtained by measuring $Nb_2O_5(s)$ solubility in concentrated nitric acid (1–6 M) giving a value of -0.6 for the equilibrium $Nb(OH)_4^+ + H_2O = Nb(OH)_5(aq) + H^+$. Guillaumont et al. (1960) calculated a value of -3.22 for this equilibrium from solvent extraction experiments. The pK linking $Nb(OH)_5$ and $Nb(OH)_6^-$ from Baes and Mesmer (7.4) differs considerably from the more reliable value that can be calculated from the Peiffert et al. (2010) data (5.0). The value 6.6 calculated by Lothenbach et al. (1999) from Yajima et al. (1992) and Yajima (1994) data was discarded by Kitamura et al. (2010) when reinterpreting the same data because they considered it was an artefact of the technique's insufficient detection limit.

A complete set of successive hydrolysis constants down to Nb^{5+} was obtained by Babko et al. (1963) who applied what these authors call the "quintuply-charged central ion-singly-charged ligand method". Even though these hydrolysis constant values are extremely dubious (and are probably devoid of any physical meaning), they have been employed subsequently (Babko et al., 1965; Volkova and Sochevanov, 1969), undermining confidence in these later results.

The interpretation of solubility data at pH > 6 differs, depending on the authors. While some of them treat it as reflecting the formation of $Nb(OH)_6^-$ (Babko et al., 1963; Lothenbach et al., 1999; Kitamura et al., 2010; Pfeiffer et al., 2010), others consider more likely the formation of the hexaniobiate anion $[H_xNb_6O_{19}]^{(8-x)-}$ (Newmann, 1964; Spinner, 1969; Goiffon et al., 1973; Etxebarria et al., 1994; Rozantsev et al., 2000; Deblonde et al., 2015b). These latter authors provide pK values for the hexaniobiate anion $[H_xNb_6O_{19}]^{(8-x)-}$ and, in some cases, other polymeric species. The Group 5 solid polyoxometalates are an active research area in inorganic chemistry but such studies are mostly of a structural nature and hence outside our present scope. In the case of niobium, the chemistry is dominated by the $[Nb_6O_{19}]^{8-}$ 'Lindqvist ion' observed both in solution and solid-state along with some coordination complexes thereof (i.e. $Mn[Nb_6O_{19}]_2^{12-}$), but there are also structural reports of the related decaniobate $[Nb_{10}O_{28}]^{6-}$ (Antonio et al., 2009; Abramov et al., 2015). Existing spectroscopic data, collected using a variety of experimental techniques, give good support for the predominance of the hexaniobiate anion.

Arana et al. (2015) combined their protonation results with solubility values from Babko et al. (1963) and calculated formation constants for the hexaniobates from $Nb(OH)_5(aq)$. However, these values depend on the solubility values of Babko and co-workers and require extrapolations outside the measurable concentration range.

Our current best estimates for Nb oxide solubility and pK values are given in Table 5 and recommended $\Delta_f G$ in Table 6.

3.2. Niobates

According to Deblonde et al. (2015b), proton equilibria for

Table 1
Published values of equilibrium constants for hydroxo complexes of niobium and solubility of niobium oxides.

Reaction	log*K*	*T*/°C	*I* electrolyte	pH range	Technique	Reference	Comments
$Nb_6O_{19}^{6-} + H^+ = HNb_6O_{19}^{5-}$	13.4 ± 0.1	25	3 M KCl	12–14.5	UV–vis	Deblonde et al. (2015b)	
$HNa_7Nb_6O_{19}.5H_2O(s) = 7\ Na^+ + HNb_6O_{19}^{7-} + 5\ H_2O$	−11.64	25	0.09–0.18 M NaCl	12	Solubility	Deblonde et al. (2015a)	
$Nb_2O_5(s) + 7\ H_2O = 2\ Nb(OH)_6^- + 2\ H^+$	−28.486	25	0.1 M NaCl	2–12	Solubility	Kitamura et al. (2010)	Data from Yajima et al. (1992) and Yajima (1994)
	−28.913		0 M				
$Nb(OH)_5(aq) + H_2O = Nb(OH)_6^- + H^+$	> −6.322		0.1 M NaCl				Values at I 0 calculated using the SIT model
	> −6.758		0 M				See comments in Table 4
$0.5\ Nb_2O_5(cr) + 1.5\ H_2O = Nb(OH)_4^+ - H^+$	−7.4 ± 0.2	25	Infinite dilution	0–9	Filtration, ICP-MS	Peiffert et al. (2010)	B–Nb_2O_5 recrystallized from commercially available oxide (Aldrich)
$0.5\ Nb_2O_5(cr) + 2.5\ H_2O = Nb(OH)_5$	−9.1 ± 0.1	Values at 10,	Values at 25 °C		(DL: 10^{-10} M)		
$0.5\ Nb_2O_5(cr) + 3.5\ H_2O = Nb(OH)_6^- + H^+$	−14.1 ± 0.3	50, 70 (*I* 1 M)	and 0.1, 0.3, 0.5,		1 g oxide per 50 mL solution		
$0.5\ Nb_2O_5(cr) + 4.5\ H_2O = Nb(OH)_7^{2-} + 2\ H^+$	−23.9 ± 0.6		1.0 M $NaClO_4$		Equilibrium: 15 days (pH < 4), 30 days (pH 4–9)		
					SIT parameters calculated		
$1/2\ H_2Nb_{12}O_{36}^{10-} + 3\ OH^- = Nb_6O_{19}^{8-} + 2\ H_2O$	17.92	25	1 M KCl	0–9	Pot/spec	Rozantsev et al. (2000)	
$1/3\ H_2Nb_{12}O_{36}^{10-} + 26/3\ OH^- = Nb_4O_{16}^{12-} + 14/3\ H_2O$	5.08						
$1/12\ H_2Nb_{12}O_{36}^{10-} + 37/6\ OH^- = NbO_6^{7-} + 19/6\ H_2O$	35.80						
$2\ H_3Nb_6O_{19}^{5-} = H_2Nb_{12}O_{36}^{10-} + 2\ H_2O$	23.46						
$2\ H_3Nb_6O_{19}^{5-} + 5\ H^+ = H_7Nb_{12}O_{36}^{5-} + 2\ H_2O$	61.03						
$2\ H_3Nb_6O_{19}^{5-} + 7\ H^+ = H_9Nb_{12}O_{36}^{3-} + 2\ H_2O$	66.84						
$2\ H_3Nb_6O_{19}^{5-} + 8\ H^+ = H_{10}Nb_{12}O_{36}^{2-} + 2\ H_2O$	78.03						
$2\ Nb(OH)_5 = Nb_2O_5(pr) + 5\ H_2O$	16	25	0.1 M NaCl	2–12	Solubility	Lothenbach et al. (1999)	Data from Yajima et al. (1992) and Yajima (1994)
$Nb(OH)_5(aq) + H_2O = Nb(OH)_6^- + H^+$	−6.6						
$Nb_6O_{19}^{8-} + H^+ = HNb_6O_{19}^{7-}$	14.29	25	0 M		Extrapolation from values at different I of Neumann (1964), Spinner (1968), Etxebarria et al. (1994)	Lothenbach et al. (1999)	
$HNb_6O_{19}^{7-} + H^+ = H_2Nb_6O_{19}^{6-}$	13.23						
$H_2Nb_6O_{19}^{6-} + H^+ = H_3Nb_6O_{19}^{5-}$	11.63						
$Nb_6O_{19}^{6-} + H^+ = HNb_6O_{19}^{5-}$	16.11 ± 0.14	25	0 M	9.7–13.1	Glass electrode, LETAGROP	Etxebarria et al. (1994)	Values for formation from 6Nb $(OH)_5$ calculated from measured constants combined with Babko et al. (1963) solubility
	13.63 ± 0.04		3 M KCl		On average the whole titration took around 7 days		
$Nb_6O_{19}^{6-} + 2\ H^+ = H_2Nb_6O_{19}^{4-}$	27.97 ± 0.13		0 M				
	23.55 ± 0.04		3 M KCl				
$Nb_6O_{19}^{6-} + 3\ H^+ = H_3Nb_6O_{19}^{3-}$	39.91 ± 0.18		0 M				
	32.90 ± 0.07		3 M KCl				
$Nb_2O_5(s) + 5\ H_2O = 2\ Nb(OH)_5$	−9.71		1 M KNO_3				Calculation of log solubility product from Babko et al. (1963)
$6\ Nb(OH)_5 - 5\ H^+ = H_3Nb_6O_{19}^{5-} + 11\ H_2O$	−14.46						
$6\ Nb(OH)_5 - 6\ H^+ = H_2Nb_6O_{19}^{6-} + 11\ H_2O$	−24.06						Extrapolation to I 0 with an extended Davies equation
$6\ Nb(OH)_5 - 7\ H^+ = HNb_6O_{19}^{7-} + 11\ H_2O$	−33.49						
$6\ Nb(OH)_5 - 8\ H^+ = Nb_6O_{19}^{8-} + 11\ H_2O$	−47.04						
$1/2\ Nb_2O_5(act) + 5/2\ H_2O = Nb(OH)_5$	≈−4.8	19	1 M KNO_3		Using previously published data	Baes and Mesmer (1976)	Calculation of Nb_2O_5(act) Ksp from Babko et al. (1953) solubility data. Values provided qualified as "only very approximate"
$Nb(OH)_5 + H^+ = Nb(OH)_4^+ + H_2O$	≈−0.6						
$Nb(OH)_5 + H_2O = Nb(OH)_6^- + H^+$	≈−7.4						
$2\ Nb_6O_{19}^{8-} + 8\ OH^- + 2\ H_2O = 3\ Nb_4O_{12}(OH)_4^{8-}$	−0.60	25	1 M KCl	1–10 M NaOH	Spectrophotometry	Goiffon et al. (1973)	
$Nb_4O_{12}(OH)_4^{8-} + 4\ OH^- + 4\ H2O = 4\ NbO_2(OH)_4^{3-}$	−11.96						
$4\ NbO_2(OH)_4^{3-} = Nb_4O_{16}^{12-} + 8\ H_2O$	8.8						
$NbO_2^+ + H_2O = NbO_2OH + H^+$	−3.2	25	0.1 M $LiClO_4$	$3–10^{-9}$ N H^+	Solvent extraction	Guillaumont et al. (1970)	
$Nb_6O_{19}^{8-} + H_2O = HNb_6O_{19}^{7-} + OH^-$	11.9	25	Infinite dilution	8–12	Glass electrode	Spinner (1968)	
$HNb_6O_{19}^{7-} + H_2O = H_2Nb_6O_{19}^{6-} + OH^-$	11.0		Values at 0.1, 0.5, 1, 2, 3 M KCl				
$H_2Nb_6O_{19}^{6-} + H_2O = H_3Nb_6O_{19}^{5-} + OH^-$	10.0						

(*continued on next page*)

Table 1 (*continued*)

Reaction	log*K*	*T*/°C	*I* electrolyte	pH range	Technique	Reference	Comments
$H_2Nb_6O_{19}^{6-} = HNb_6O_{19}^{7-} + H^+$	−10.88 ± 0.05	25	3 M KCl	10.7–12.25	Hydrogen electrode	Neumann (1964)	Initial product: $K_7HNb_6O_{19}$
$HNb_6O_{19}^{7-} = Nb_6O_{19}^{8-} + H^+$	−13.8 ± 0.2						
$Nb(OH)_5 = Nb(OH)_4^+ + OH^-$	−14.6	18:20	1 M KNO_3	0–10	Solubility	Babko et al. (1963)	Isoelectric range: pH 0–7
$Nb(OH)_5 = NbO_3^- + H^+ + 2\ H_2O$	−7.4				2–3 weeks equilibration		They measured the solubility
$Nb^{5+} + OH^- = Nb(OH)^{4+}$	33.2				Centrifugation and photometric		of "freshly precipitated
$Nb(OH)^{4+} + OH^- = Nb(OH)_2^{3+}$	29.8				Nb determination (xylenol		niobium hydroxide" (Nb
$Nb(OH)_2^{3+} + OH^- = Nb(OH)_3^{2+}$	25.2				orange)		$(OH)_5(s)$): 1.4×10^{-5} M
$Nb(OH)_3^{2+} + OH^- = Nb(OH)_4^+$	19.9						They applied the "quintuply-charged centrail ion-singly charged ligand" method to calculate hydrolysis constants from Nb^{5+} to $Nb(OH)_4^+$

hexaniobate should be seen as an exchange between alkali ions and protons rather than a simple proton release because of extensive ion pairing between alkali ions and hexaniobate. Ion-pairing shows marked differences depending on the cation, with Cs > Rb > K > Na > Li (Antonio et al., 2009; Nyman et al., 2006). The effect on protonation was confirmed by these authors who found (as is usually expected) that protonation in NaCl/NaOH media gave lower protonation constants than in KCl/KOH media. Further work by Deblonde and co-workers (Deblonde et al., 2015a) led to the determination of the solubility product for $Na_7HNb_6O_{19}.15H_2O(s)$ which, according to these authors, is the solubility limiting phase in sodium-containing alkaline media (rather than the simple oxide).

Hydrated and anhydrous sodium (Beford, 1905), potassium (Marignac, 1866) and lithium (Balke and Smith, 1908) niobates have been known for a long time but sound values for their solubility are lacking. Standard Gibbs free energy of formation, $\Delta_f G^o$, for $NaNbO_3(c)$, $Na_3NbO_4(c)$, $KNbO_3(c)$, $K_3NbO_4(c)$ and $Ca(NbO_3)_2(c)$, extracted from third-party compilations, were reported by Lothenbach et al. (1990) but they did not attempt to calculate a solubility product from these values and no thermodynamic values for the formation of these solids were recommended.

3.3. Fluoride

Although the refining technology of niobium involves niobium fluoride (Agulyansky, 2004), equilibrium constants for this system have been measured in only a very limited number of studies (Babko et al., 1967; Erskine et al., 1969; Neumann, 1970; Land and Osborne, 1972; Hammer, 1979; Timofeev et al., 2015). Most of them have been performed with high fluoride concentrations and under very acidic conditions (Table 3). They cannot be used to predict niobium complexation by fluoride in hydrothermal fluids (Wood, 2004), and even less so under environmental or biological conditions. Knowing the true identity of the complexes formed is another frequent limitation. Ternary (or 'mixed ligand') complexes of the type $Nb(OH)_{n-m}F_m^{5-n}$ are highly likely but it is more than difficult to measure the effect of OH^- groups leaving the niobium ion using a fluoride electrode under highly acid conditions. Hammer et al. (1979), for instance, were unable to determine the composition of the complexes formed and their proposed constants cannot sensibly be used for thermodynamic calculations. Formation of complexes $NbOF_5^{2-}$ and NbF_6^- have been detected by infrared and or Raman spectroscopy (Keller, 1963; Griffith and Wickins, 1967; Tsikaeva et al., 1989) in very concentrated HF solutions (e.g., $NbOF_5^{2-}$ in 5 M HF in Griffith and Wickins, 1967) but these data are of little value when trying to understand the complexation of fluoride under much milder pH and fluoride concentration conditions.

Timofeev et al. (2017) measured the solubility of $Nb_2O_5(cr)$ in HF-containing solutions at pH < 3.1, high temperatures (100–250 °C) and saturated vapour pressure. Interestingly, they found formation of $Nb(OH)_4^+$ and no complexation by fluoride at low HF concentrations (<0.001 m HF) and formation of $NbF_2(OH)_3$ at higher HF values. These results strongly suggest that at low fluoride concentrations, niobium is not complexed by fluoride and that, at higher concentrations, only ternary complexes are formed.

3.4. Other inorganic equilibria

Complex formation between niobium and carbonate at high temperature and pressure conditions has not received any attention (Aleksandrov, 1967) and to our knowledge no equilibrium constants have been reported.

A theoretical study predicted that the formation of the complexes $Nb(OH)_2Cl_4^-$, $NbOCl_4^-$ and $NbCl_6^-$ when chloride concentrations increase in aqueous solution (Pershina, 1998). Niobium equilibria with chloride have been studied by several authors (Huffman et al., 1951; Kanzelmeyer et al., 1956; Griffith and Wickins, 1967; Davies and Long, 1968)

Table 2
Published values of equilibrium constants for fluoride complexes of niobium.

Reaction[a]	logK^a	T/°C	I electrolyte	pH range	Technique	Reference	Comments
$Nb_2O_5(s) + 2\ H^+ + 3\ H_2O = 2\ Nb(OH)_4^+$	-11.23 ± 0.26	150	3 M $NaClO_4$	1.6–3.1	Solubility	Timofeev et al. (2015)	Synthetic $Nb_2O_5(s)$ (Alfa Aesar)
	-10.83 ± 0.37	200			Nb measurement: ICP-MS (DL: not given)		
	-11.86 ± 0.24	250			Equilibration: 6 days		
$Nb_2O_5(s) + 4\ HF + H_2O = 2\ NbF_2(OH)_3$	-3.84 ± 0.20	150					
	-4.04 ± 0.22	200					
	-5.08 ± 0.42	250					
$Nb(OH)_n^{5-n} + HF = Nb(OH)_{n-1}F^{5-n} + H_2O$	2.13	25	0.96 M HNO_3	0.96, 2.88 M H^+	potentiometry	Hammer (1979)	As cited by Wood (2004); this author mentioned that it is unclear whether the hydroxyde specied involved where mono- or polynuclear
	2.01	25	2.88 M HNO_3				
	2.06	35	0.96 M HNO_3				
	1.96	35	2.88 M HNO_3				
	1.79	45	0.96 M HNO_3				
$Nb(OH)_n^{5-n} + 2\ HF = Nb(OH)_{n-2}F_2^{5-n} + 2\ H_2O$	4.00	25	0.96 M HNO_3				
	4.23	25	2.88 M HNO_3				
	3.30	35	0.96 M HNO_3				
	3.04	35	2.88 M HNO_3				
	3.40	45	0.96 M HNO_3				
$Nb(OH)_n^{5-n} + 3\ HF = Nb(OH)_{n-3}F_3^{5-n} + 3\ H_2O$	5.86	25	0.96 M HNO_3				
	5.81	25	2.88 M HNO_3				
	5.30	35	0.96 M HNO_3				
	5.3	35	2.88 M HNO_3				
	5.40	45	0.96 M HNO_3				
$Nb(OH)_n^{5-n} + 4\ HF = Nb(OH)_{n-4}F_4^{5-n} + 4\ H_2O$	8.66	25	0.96 M HNO_3				
	8.66	25	2.88 M HNO_3				
	8.57	35	0.96 M HNO_3				
	8.47	35	2.88 M HNO_3				
	8.41	45	0.96 M HNO_3				
$NbOF_2^+ + F^- = NbOF_3$	3.78	25	0.5 M $NaClO_4$	0.08–0.18 M H^+	Fluoride selective electrode	Land and Osborne (1972)	Initial product: $K_2NbOF_5.H_2O$ (Alfa Inorganics)
$NbOF_3 + F^- = NbOF_4^-$	4.30						For T_H/T_M ratios higher than 175, only $NbF_n^{(5-n)}$ species formed
$NbOF_4^- + F^- = NbOF_5^{2-}$	4.50						
$NbOF_5^{2-} + F^- = NbOF_6^{3-}$	4.67						
$NbOF_6^{3-} + 2\ H^+ + F^- = NbF_7^{2-} + H_2O$	11.4						
$NbF_7^{2-} + F^- = NbF_8^{3-}$	3.1						
$NbF_8^{3-} + F^- = NbF_9^{4-}$	4.0						
$NbF_5 + 2\ F^- = NbF_7^{2-}$	10.66	25	5.0 M (Na,H)ClO_4	2–5 M H^+	Solvent extraction	Erskine et al. (1969)	Initial product: 10^{-12} M carrier free ^{95}Nb
							"The initial assumption was made that only non-hydrolysed, mononuclear species were present"
$Nb(OH)_2F_4^- + F^- = Nb(OH)_2F_5^{2-}$	2.51 ± 0.03	25	3 M KCl	1–4	Quinhydrone and fluoride electrodes	Neumann (1970)	Initial product: $K_7Nb_6O_{19}.(H_2O)_n$, n = 13,14
$Nb(OH)_3F_2 + HF = Nb(OH)_2F_3 + H_2O$	4.2		3 M HNO_3	3 N HNO_3	Solubility; Nb measured by colorimetry (xylenol orange)	Babko et al. (1967)	Initial product: freshly precipitated $Nb(OH)_5(s)$
$Nb(OH)_4F + HF = Nb(OH)_4F_2^- + H^+$	3.6		0.5 M HNO_3	pH: 0–2			$Nb(OH)_3F_2$ solubility: 1.5×10^{-5} M (3 N HNO_3)
$Nb(OH)_4F + F^- = Nb(OH)_4F_2^-$	6.8						$Nb(OH)_4F$ solubility: 0.6×10^{-5} M (pH 1)

Table 3
Published values of equilibrium constants for low molecular weight organic complexes of niobium.

Ligand	Reaction[a]	log*K*[a]	*T*/°C	*I* electrolyte	pH range	Technique	Reference	Comments
Citrate (L^{2-})	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	2.92 2.95	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	
EDTA (L^{4-})	$Nb(OH)_5 + L^{4-} = Nb(OH)_2L^- + 3\ OH^-$ or $Nb(OH)_2^{3+} + L^{4-} = Nb(OH)_2L^-$ Or $Nb(OH)_5 + H_4L = Nb(OH)_2L^- + 3\ H_2O + H^+$	40.78	20	1.08 M K_2SO_4	2–5	Polarography Initial reaction mixture obtained by boiling	Volkova and Sochevanov (1967)	Follows Babko et al. (1963) using "quintuply-charged centrail ion-singly charged ligand" estimated hydrolysis constants Second reaction: as understood by Sillén and Martell (1971) Third reaction follows the way the authors wrote the same reaction for Ta (Volkova and Sochevanov (1969)
EDTA (L^{4-})	No reaction written	40	?	0.4 M KCl	3.5	Polarography	Sochevanov and Volkova (1969)	
Malate (L^{2-})	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	2.02 2.00	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	
Malonate (L^{2-})	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	1.74 1.71	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	
Oxalate (L^{2-})	$NbOL_3^{3-} = NbOL_2^- + L^{2-}$	6.17 ± 0.4	20	Self medium	0.3–1.8	Solubility Radioactive isotopes (^{95}Nb) 2 h equilibration	Zhurenkov and Pobezhimovskaya (1970)	
Oxalate (L^{2-})[a]	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	3.48 3.61	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	
	$Nb(OH)_4^+ + 2\ H_2L = Nb(OH)_2L_2^- + 2\ H^+$	5.18 5.09		4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3				
Oxalate (L^{2-})	$Nb(OH)_5(s) + 3\ H^+ + 2\ L^{2-} = Nb(OH)_2L_2^- + 3\ H_2O$ $Nb(OH)_5(s) + 3\ H^+ + 3\ L^{2-} = Nb(OH)_2L_3^{3-} + 3\ H_2O$	12.1 17.15	25	0.5 M KNO_3 or $NaClO_4$	0.45–5.04	Potentiometry	Nevzorov and Songina (1967)	Precipitation of Nb$(OH)_5$(s) starts at pH 3.5, complete at pH 7 Calculation in presence of precipitate
Salicylate (L^{2-})	$NbO^{3+} + 2\ L^{2-} = NbOL_2^-$	22.6	25	0.04 M	3.9	Spectrophotometry	Babko and Volkova (1962)	"These data are only approximate, since the state in solution of uncombined niobium is unknown"
Succinate (L^{2-})	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	1.48 1.58	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	
Tartrate ($L^{?-}$)	$Nb(OH)_4^+ + H_2L = Nb(OH)_4HL + H^+$	2.34 2.33	20	4.5 M (H, Na)Cl 4.5 M (H, Na)NO_3	0.3–1.8	Solvent extraction Samples shaken 24 h	Konečný (1967)	

[a] In this case, the interpretation of the reactions by Sillén and Martell (1971) has been followed.

Table 4
Experimental conditions in solubility studies of niobium oxides.

Reference	Analytical method	Detection limit	Solubility measured in the zone pH < 6/mol L^{-1}	Solid preparation	Solid characterisation
Deblonde et al. (2015a)	ICP-OES	0.5 mg L^{-1}	$<5.4 \times 10^{-6}$	56-d aged (25 °C) $Nb_2O_5.nH_2O$ prepared by hydrolysing $NbCl_5$(s) in water at pH 4 (adjusted with NaOH)	XRD
Timofeev et al. (2015)	ICP-MS	Not given	$\sim 10^{-7.8}$ at 150 °C, pH ~2	Synthetic Nb_2O_5(s) (Alfa Aesar)	No
Pfeiffer et al. (2010)	ICP-MS	1×10^{-10} mol L^{-1}	$\sim 10^{-9}$	Aldrich Nb_2O_5(s) heated up to 1000 °C at 0.1 Mpa for 10 h	XRD: confirmed B–Nb_2O_5 (monoclinic), SEM: size range 5–10 μm
Yajima (1994) [a]	ICP-MS	Not given but better than in Yajima et al. (1992) [c]	1×10^{-8} [c]	Under- and oversaturation after 7 and 28 d	XRD but results not available (see text)
Yajima et al. (1992) [a]	ICP-OES	Not given	[b]	Under and oversaturation after 7 and 28 d	XRD but results not available (see text)
Babko et al. (1963)	Centrifugation Photometric: xylenol orange	Not given	1.4×10^{-5}	*In situ* precipitation: addition of HNO_3 to an alkaline solution of $KNbO_3$	No

[a] Information from Lothenbach et al. (1999) and Kitamura et al. (2010).
[b] Used by Lothenbach et al. (1999) but only values at pH > 7 used by Kitamura et al. (2010) because analytical detection limit judged insufficient.
[c] Solubility values around the detection limit need to be treated as "a maximum value", according to Kitamura et al. (2010).

Table 5
Best stability constant values for niobium species, 25 °C and infinite dilution.[a]

Reaction	$\log K^0$
$Nb(OH)_5(am.,s) = Nb(OH)_5^0$	−7.510
$Nb_2O_5(s) + 5\ H_2O = 2\ Nb(OH)_5^0$	−18.31
$Nb(OH)_5^0 + H^+ = Nb(OH)_4^+ + H_2O$	1.603
$Nb(OH)_5^0 + H_2O = Nb(OH)_6^- + H^+$	−4.951
$Nb_6O_{19}^{8-} + H^+ = HNb_6O_{19}^{7-}$	14.95
$HNb_6O_{19}^{7-} + H^+ = H_2Nb_6O_{19}^{6-}$	13.23
$H_2Nb_6O_{19}^{6-} + H^+ = H_3Nb_6O_{19}^{5-}$	11.73
$HNa_7Nb_6O_{19}.5H_2O(s) = 7\ Na^+ + HNb_6O_{19}^{7-} + 5\ H_2O$	−17.79
$Nb(OH)_5^0 + 2\ F^- + 2\ H^+ = NbF_2(OH)_3^0$	11.85

[a] Five significant figures are retained to minimise propagation of round-off errors, typically caused by subtractions between two such large numbers; the number of significant figures should not be taken to indicate the relative uncertainty of the values, which is always at least an order of magnitude less than indicated (see text).

Table 6
Recommended $\Delta_f G^0$ for niobium species.[a]

Species	$\Delta_f G^0$ (kJ mol^{-1})
$Nb(OH)_5(am.,s)$	−1467.7
$Nb_2O_5(s)$	−1768.3
$Nb(OH)_5^0$	−1424.9
$Nb(OH)_6^-$	−1633.8
$Nb(OH)_4^+$	−1196.8
$Nb_6O_{19}^{8-}$	−5609.3
$HNb_6O_{19}^{7-}$	−5694.6
$H_2Nb_6O_{19}^{6-}$	−5770.1
$H_3Nb_6O_{19}^{5-}$	−5837.1
$HNa_7Nb_6O_{19}.5H_2O(s)$	−8815.3
$NbF_2(OH)_3^0$	−1580.6

[a] Five significant figures are retained to minimise propagation of round-off errors, typically caused by subtractions between two such large numbers; the number of significant figures should not be taken to indicate the relative uncertainty of the values, which is always at least an order of magnitude less than indicated (see text).

but none of them reported equilibrium constant values. All these studies were performed with very high HCl concentrations.

Equilibrium constants for polynuclear complexes formed in 1–8 M H_2SO_4(aq) solutions at 70 °C were reported by Ivanenko et al. (1996) but it is unclear how the stoichiometries proposed were determined. An

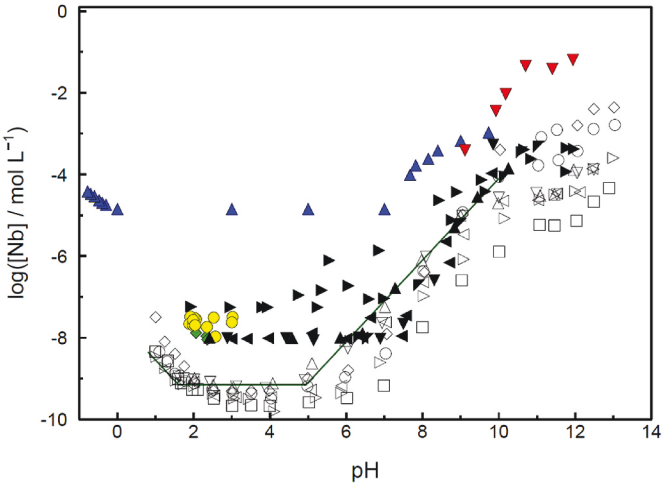

Fig. 1. Solubility of niobium oxide. "Freshly precipitated niobium hydroxide", 18–20 °C (Babko et al., 1963) in blue; 56-day aged niobium hydroxide, 25 °C (Deblonde et al., 2015a) in red; commercial Nb_2O_5(s) at 150 and 200 °C (Timofeev et al., 2017) in yellow and green, respectively. Empty symbols correspond to values from Peiffert et al. (2010) for monoclinic B–Nb_2O_5 and filled black ones to data from Yajima et al. (1992) and Yajima (1994). Different symbols correspond to different experimental conditions. Solid green line calculated with values in Table 5 for Nb_2O_5(s). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

equilibrium constant value has been reported for the complexation of niobium with sulfate but for a species of undefined stoichiometry, $Nb(OH)_mSO_4^{3-m}$ (Pevsner and Sheka, 1968).

Accordingly, no equilibrium constant values for any inorganic ligand other than fluoride can be considered available for any practical purpose.

3.5. Organic ligands

Tartaric, oxalic and citric acid have been used in 'traditional' analytical chemistry to prepare stable solutions of niobium (Moshier, 1964) although this requires the treatment of 'freshly precipitated niobic acid', which must be prepared by the addition of ammonia in solution, together with hot solutions of the ligands. This type of procedure is also

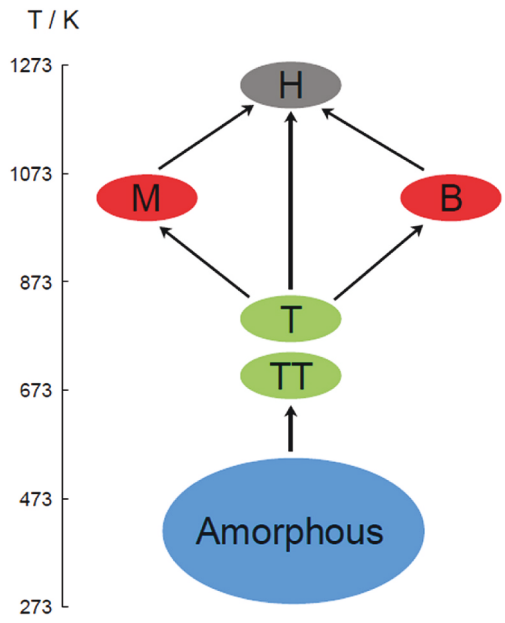

Fig. 2. Niobium oxides and their phase transitions. Crystalline phases: T (orthorhombic), TT (pseudohexagonal or monoclinic), B (monoclinic), M (tetragonal) and H (monoclinic). Adapted from Pinto et al. (2017).

followed for the synthesis of niobates in a technological setting (Camargo et al., 2002; Ali and Gates, 2018). The relative complexation capability of organic ligands for niobium has accordingly been studied for a long time. As early as 1950, Haïssinsky and Yang (1950) reported that the resistance to hydrolysis of the complexes decreased in the order: oxalate > citrate > tartrate. The reactivity of niobic acid with the α-hydroxy-acids glycollic, lactic, malic, and citric was studied in detail by Fairbrother and Taylor (1956) and the solid 1:1 complexes isolated. Their preparation required chemically harsh methods (such as refluxing for 24 h) and the complexes were reported to be stable in aqueous solution only in the presence of ligand excess. No reaction was observed with malonic, succinic, adipic, or phthalic acids. More recently, Radchenko et al. (2014) analysed different chelators in terms of the distribution of radioactivity of ^{95}Nb between a cation exchange resin (Chelex) and the complexes. They reported TTHA, DTPA and EDTA having "good complexation properties" at pH 4.7 over a period of 24 h. Others (CDTA, DOTA, TETA and PAR) were less efficient complexants and the cyclic chelators (DOTA and TETA) required heating for 3 h at 60 °C due to the slow reaction kinetics.

Equilibrium constants for the complexation of niobium by certain l.m.m. organic ligands were measured in the 1960's. They span a limited number of ligands: citrate (Konecky, 1967), EDTA (Konečný, 1967; Zhurenkov and Pobezhimovskaya, 1970), malate (Konečný, 1967), malonate (Konečný, 1967), oxalate (Babko and Volkova, 1962; Konečný, 1967; Nevzorov and Songina, 1967), salicylate (Konečný, 1967) and succinate (Konečný, 1967). It is difficult to evaluate the validity and usefulness of these results. Interpretation of the results is hampered by confused reporting, studies being confined only to acidic conditions, possible presence of unsuspected solid phases, and an ambiguous number of hydroxyl groups present in the reacting species. The reported reactions and values, as stated by these authors, can be found in Table 4. However, evident in the entry of Volkova and Sochevanov (1967) for EDTA, different interpretations are often possible. It is not feasible at present to give a set of constants that are suitable for modelling calculations.

4. Conclusions

As is the case for tantalum (Filella and May 2019), niobium equilibria in aqueous solution have not been adequately studied. In particular, the solubility of niobium oxide is generally uncertain because of the many possible polymorphs that can be formed. Moreover, those few values which have been published seem to be strongly dependent on the detection limit of the analytical technique used. The use of current analytical ICP-MS capabilities, with detection limits around 1×10^{-12} mol L^{-1} (Filella et al., 2014), has the potential to liberate the determination of niobium's solubility from analytical constraints and focus on the adequate characterisation of the solid phases and on the critical issue of kinetics. The situation with niobium solubility studies provides a good example of the difficulties arising with solubility studies but also of the need to control and document the solid phases studied. This requirement is particularly important when dealing with rapidly-changing amorphous phases.

Published solubility values do not indicate any solubility control of niobium concentrations in natural waters where concentrations occur around 4×10^{-11} mol L^{-1} in fresh water (European freshwaters, FOREGS project, Salminen et al. (2005)) and ~2×10^{-12} mol L^{-1} in ocean water (Firdaus et al., 2011; Poehle and Koschinsky, 2017). Interestingly, the niobium concentration measured in a bottled water from a volcanic area (Eiffel, Germany), 4.5×10^{-9} mol L^{-1} (Filella et al., 2014), suggests that the concentration of niobium in this exceptional case might be solubility controlled. High niobium concentrations have been found routinely in zones influenced by volcanism (Salminen et al., 2005).

The explanation of niobium behaviour in some waters being determined by complexation to fulvic and humic acids (Salminen et al., 2005) remains doubtful in our opinion considering the specific conditions required for niobium complexation by ligands such as oxalic or citric acids. Similar arguments apply to tantalum. Even though desferrioxamine (DFO) has been found to be a good chelator of ^{90}Nb in a radiopharmaceutical-related study (Radchenko et al., 2014), the assignment of niobium behaviour in the deep Pacific ocean to siderophore complexation (Poehle and Koschinsky, 2017) remains questionable. In any case, there are no equilibrium constants available to enable quantitative prediction of these processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2020.104729.

References

Abramov, P.A., Sokolov, M.N., Vicent, C., 2015. Polyoxoniobates and polyoxotantalayes as ligands – Revisited. Inorganics 3, 160–177.
Agulyansky, A., 2004. Chemistry of Tantalum and Niobium Fluoride Compounds. Elsevier, Amsterdam.
Aleksandrov, I.V., 1967. Niobium in the carbonate solutions and some considerations on the migration of rare elements under hydrothermal conditions. Geochem. Int. 4, 558–566.
Ali, R.F., Gates, B.D., 2018. Synthesis of lithium niobate nanocrystals with size focusing through an Ostwald ripening process. Chem. Mater. 30, 2028–2035.
Antonio, M.R., Nyman, M., Anderson, T.M., 2009. Direct observation of contact ion-pair formation in aqueous solution. Angew. Chem. Int. Ed. 48, 6136–6140.
Babko, A.K., Lukachina, V.V., Nabivanets, B.L., 1963. Solubility and acid-base properties of tantalum and niobium hydroxides. Russ. J. Inorg. Chem. 8, 957–961.
Babko, A.K., Nabivanets, B.L., Lukachina, V.V., 1967. Interaction of hydrated niobium pentoxide with hydrofluoric acid. Russ. J. Inorg. Chem. 12, 1568–1572.
Babko, A.K., Volkova, A.I., 1962. Complex-formation in niobium(V)-salicylate-organic base systems. Russ. J. Inorg. Chem. 7, 1216–1220.
Baes, C.F., Mesmer, R.E., 1976. The Hydrolysis of Cations. Wiley, New York.
Balke, C.W., Smith, E.F., 1908. Observations on columbium. J. Am. Chem. Soc. 30, 1637–1668.
Bedford, M.H., 1905. Columbates. J. Amer. Chem. Soc. 27, 1216–1221.

Byrne, R.H., 2002. Inorganic speciation of dissolved elements in seawater: the influence of pH on concentration ratios. Geochem. Trans. 3, 11–16.
Davies, J.E.D., Long, D.A., 1968. The vibrational spectra of titanium tetrachloride–hydrochloric acid and titanium tetrachloride–tri-n-butyl phosphate systems and the hexachloro-anions of zirconium(IV), hafnium(IV), niobium(V), and tantalum(V). J. Chem. Soc. A 2560–2564.
Deblonde, G.J.-P., Chagnes, A., Bélair, S., Cote, G., 2015a. Solubility of niobium(V) and tantalum(V) under mild alkaline conditions. Hydrometallurgy 156, 99–106.
Deblonde, G.J.-P., Moncomble, A., Cote, G., Bélair, S., Chagnes, A., 2015b. Experimental and computational exploration of the UV-visible properties of hexaniobate and hexatantalate ions. RSC Adv. 5, 7619–7627.
Erskine, J.S., Sink, M.L., Varga, L.P., 1969. Solvent extraction separation of tantalum and niobium fluorides with *N*-benzoyl-*N*-phenylhydroxylamine. Anal. Chem. 41, 70–73.
Etxebarria, N., Fernández, L.A., Madariaga, J.M., 1994. On the hydrolysis of niobium(V) and tantalum(V) in 3 mol dm^{-3} KCl at 25 C. Part 1. Construction of a thermodynamic model for Nb(V). J. Chem. Soc., Dalton Trans. 3055–3059.
Fairbrother, F., Taylor, J.B., 1956. Water-soluble complexes of niobium (columbium) and tantalum. Part I. Complexes with α-hydroxy-acids and (2-hydroxyethyl)-amines. J. Chem. Soc. 4946–4954.
Filella, M., Magnenat, D.-J., Bensimon, M., 2014. Direct determination of niobium at the low nanogram level in mineral waters and freshwaters. Anal. Methods 6, 8090–8093.
Filella, M., May, P.M., 2019. The aqueous solution thermodynamics of tantalum under conditions of environmental and biological interest. Appl. Geochem. 109, 104402.
Firdaus, M.L., Minami, T., Norisuye, K., Sohrin, Y., 2011. Strong elemental fractionation of Zr–Hf and Nb–Ta across the Pacific ocean. Nat. Geosci. 4, 227–230. https://doi.org/10.1038/ngeo1114.
Goiffon, A., Granger, R., Bockel, C., Spinner, B., 1973. Study of the equilibria in alkaline solutions of Nb V. Rev. Chim. Miner. 10, 487–502 [in French] (Etude des équilibres dans les solutions alcalines du niobium V).
Griffith, W.P., Wickins, T.D., 1967. Raman studies on species in aqueous solutions. Part II. Oxy-species of metals of Groups VIA, VA, and IVA. J. Chem. Soc. A 675–679.
Guillaumont, R., Franck, J.C., Muxart, R., 1970. Contribution to the study of the hydrolysis of niobium. Radiochem. Radioanal. Lett. 4, 73–79 [in French] (Contribution à l'étude de l'hydrolyse du niobium).
Gunn, G. (Ed.), 2014. Critical Metals Handbook. American Geophysical Union and Wiley, Nottingham, UK.
Haïssinsky, M., Yang, J.-T., 1950. On the stability of some organic complexes of the elements of the fourth and fifth groups of the periodic system: oxalates, citrates and tartrates of Nb, Ta and Pa. Anal. Chim. Acta 4, 328–332 [in French] (Sur la stabilité de quelques complexes organiques des éléments des quatrième et cinquième groupes du système périodique: oxalates, citrates et tartrates de Nb, Ta et Pa).
Hammer, R.R., 1979. A Determination of the Stability Constants of a Number of Metal Fluoride Complexes and Their Rates of Formation. USDOE Report, Idaho Chemical Processing Plant. EXXON Nuclear Idaho Company. ENICO 1004 (as cited by Wood, 2004).
Huffman, E.H., Iddings, G.M., Lilly, R.C., 1951. Anion exchange of zirconium, hafnium, niobium and tantalum in hydrochloric acid solutions. J. Am. Chem. Soc. 73, 4474–4475.
Ivanenko, V.I., Kadyrova, G.I., Kravtsov, V.I., 1996. Niobium (V) polynuclear complexes in sulfuric acid solutions. Russ. J. Appl. Chem. 69, 13–16.
Kanzelmeyer, J.H., Ryan, J., Freund, H., 1956. The nature of niobium(V) in hydrochloric acid solution. J. Am. Chem. Soc. 78, 3020–3023.
Keller Jr., O.L., 1963. Identification of complex ions of niobium(V) in hydrofluoric acid solutions by Raman and infrared spectroscopy. Inorg. Chem. 2, 783–787.
Kitamura, A., Fujiwara, K., Doi, R., Yoshida, Y., Mihara, M., Terashima, M., Yui, M., 2010. JAEA Thermodynamic Database for Performance Assessment of Geological Disposal of High-Level Radioactive and TRU-Wastes. Report JAEA-Data/Code 2009-024. Japan Atomic Energy Agency, p. 84.
Konečný, C., 1967. Studies on complex formation by solvent extraction method. II. Niobium(V) complexes in aqueous solution. Z. Phys. Chem. 235, 39–48.
Land, J.E., Osborne, C.V., 1972. The formation constants of the niobium fluoride system. J. Less Common. Met. 29, 147–153.
Lothenbach, B., Ochs, M., Wanner, H., Yui, M., 1999. Thermodynamic Data for the Speciation and Solubility of Pd, Pb, Sn, Sb, Nb and Bi in Aqueous Solution. Japan Nuclear Cycle Development Institute (JNC). TN8400 99-011.
Marignac, M.C., 1866. Research on combinations of niobium. Ann. Chem. Phys. 4, 5–75 [in French] (Recherches sur les combinaisons du niobium).
May, P.M., 2000. A simple, general and robust function for equilibria in aqueous electrolyte solutions to high ionic strength and temperature. Chem. Commun. (J. Chem. Soc. Sect. D) 1265–1266.
May, P.M., Rowland, D., 2018. JESS, a joint expert speciation system - VI: thermodynamically-consistent standard Gibbs energies of reaction for aqueous solutions. New J. Chem. 42, 7617–7629.
Moshier, R.W., 1964. Analytical Chemistry of Niobium and Tantalum. The Macmillan Company, New York.
Nevzorov, A.N., Songina, O.A., 1967. The state of niobium in oxalic acid solutions. Russ. J. Inorg. Chem. 12, 1259–1262.
Neumann, G., 1964. On the hydrolysis of niobates in 3 M K(Cl) medium. Acta Chem. Scand. 18, 278–280.
Neumann, G., 1970. A potentiometric study of the system Nb(V)-OH^--F^- in 3 M K(Cl) medium. Ark. Kemi. 32, 229–247.
Nyman, M., Alam, T.M., Bonhomme, F., Rodriguez, M.A., Frazer, C.S., Welk, M.E., 2006. Solid-state structures and solution behavior of alkali salts of the $[Nb_6O_{19}]^{8-}$ Lindqvist ion. J. Cluster Sci. 17, 197–219.
Paquet, N., Indiketi, N., Dalencourt, C., Larivière, D., Roberge, S., Gruyer, N., Triffault-Bouchet, G., Fortin, C., 2019. Toxicity of tailing leachates from a niobium mine toward three aquatic organisms. Ecotoxicol. Environ. Saf. 176, 355–363.
Peiffert, C., Nguyen-Trung, C., Palmer, D.A., Laval, J.P., Giffaut, E., 2010. Solubility of B-Nb_2O_5 and the hydrolysis of niobium(V) in aqueous solution as a function of temperature and ionic strength. J. Solut. Chem. 39, 197–218.
Pershina, V., 1998. Solution chemistry of element 105 Part II: hydrolysis and complex formation of Nb, Ta, Ha and Pa in HCl solutions. Radiochim. Acta 80, 75–84.
Pevsner, T.V., Sheka, I.A., 1968. Reaction of niobium and tantalum with sulphate ions in solution. Russ. J. Inorg. Chem. 13, 1381–1384.
Pinto, M.B., Soares Jr., A.L., Orellana, A.M., Duarte, H.A., De Abreu, H.A., 2017. Structural, electronic, and thermodynamic properties of the T and B phases of niobia: first-principle calculations. Phys. Chem. 121, 2399–2409.
Poehle, S., Koschinsky, A., 2017. Depth distribution of Zr and Nb in seawater: the potential role of colloids or organic complexation to explain non-scavenging-type behavior. Mar. Chem. 188, 18–32.
Radchenko, V., Busse, S., Roesch, F., 2014. Desferrioxamine as an appropriate chelator for ^{90}Nb: comparison of its complexation properties for M-Df-Octreotide (M = Nb, Fe, Ga, Zr). Nucl. Med. Biol. 41, 721–727.
Rozantsev, G.M., Dotsenko, O.I., Taradina, G.V., 2000. Mathematical modeling and analysis of equilibria in solutions of Nb(V). Russ. J. Coord. Chem. 26, 247–253.
Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. Geochemical atlas of europe. In: Part 1: Background Information, Methodology and Maps. Geological Survey of Finland, Espoo, p. 526 (Chief-editor)).
Schäfer, H., Gruehn, R., Schulte, F., 1966. The modifications of niobium pentoxide. Angew. Chem., Int. Ed. Engl. 5, 40–52.
Schulz, K.J., Piatak, N.M., Papp, J.F., 2017. Niobium and tantalum, chap. M of Schulz. In: J, K., DeYoung Jr., J.H., Seal II, R.R., Bradley, D.C. (Eds.), Critical Mineral Resources of the United States—Economic and Environmental Geology and Prospects for Future Supply: U.S. Geological Survey Professional Paper 1802, pp. M1–M34. https://doi.org/10.3133/pp1802M.
Sochevanov, V.G., Volkova, G.A., 1969. Use of polarography in the determination of the instability constants of complexonates of readily hydrolysable elements. Russ. J. Inorg. Chem. 61–64.
Spinner, B., 1968. Quantitative study of the hydrolysis of the potassium niobates. Rev. Chim. Miner. 5, 839–868 [in French] (Étude quantitative de l'hydrolyse des niobates de potassium).
Sillén, L.G., Martell, A.E., 1971. Stability Constants of Metal-Ion Complexes SP25. Supplement No. 1 to Special Publication No. 25. The Chemical Society, London.
Timofeev, A., Migdisov, A.A., Williams-Jones, A.E., 2015. An experimental study of the solubility and speciation of niobium in fluoride-bearing aqueous solutions at elevated temperature. Geochem. Cosmochim. Acta 158, 103–111.
Tsikaeva, D.V., Agulyanskii, A.I., Balabanov, YuI., Kuznetsov, V.Ya, Kalinnikov, V.T., 1989. Complexation of niobium(V) in hydrofluoric acid solutions in the presence of fluorides of alkali metals and ammonium. Russ. J. Inorg. Chem. 34, 1740–1744.
Volkova, G.A., Sochevanov, V.G., 1967. Complex formation by niobium hydroxide with EDTA. Russ. J. Inorg. Chem. 12, 222–225.
Volkova, G.A., Sochevanov, V.G., 1969. Reaction of tantalum-hydroxide with ethylenediaminetetra-acetic acid. Russ. J. Inorg. Chem. 14, 652–654.
Wood, S.A., 2004. The aqueous geochemistry of zirconium, hafnium, niobium and tantalum. In: Linnen, R.L., Samson, I.M. (Eds.), Rare-Element Geochemistry and Mineral Deposits. Geological Association of Canada Short Course Notes 17, St. Catharines, Ontario, pp. 217–268.
Yajima, T., 1994. Solubility Measurements of Uranium and Niobium, Report of Yayoi Kenkyukai, UTNL-R 0331. University of Tokyo, pp. 127–144 [in Japanese] (as cited by Kitamura et al. 2010).
Yajima, T., Tobita, S., Ueta, S., 1992. Solubility measurements of niobium in the system Nb-O-H under CO_2-free condition. In: Presented at 1992 Fall Meeting of Atomic Energy Society of Japan, F33, p. 341 [in Japanese] (as cited by Kitamura et al. 2010).
Zhurenkov, E.M., Pobezhimovskaya, D.N., 1970. Determination of the composition and instability constants of oxalate complexes of niobium and tantalum by the solubility method. Radiochemistry 12, 89–94.

Abbreviations

CDTA: 1,2-Cyclohexylenedinitrilotetraacetic acid
DFO: Desferrioxamine
DOTA: 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid
DTPA: Diethylenetriaminepentaacetic acid
EDTA: Ethylenediaminetetraacetic
ICP-MS: Inductively coupled plasma mass spectrometry
ICP-OES: Inductively coupled optical emission spectrometry
PAR: 4-(2-Pyridinylazo)-1,3-benzenediol
TETA: Triethylenetetramine
TTHA: 3,6,9,12-Tetraazatetradecanedioic acid