

Springer Mineralogy

Yuriy Litvin  
Oleg Safonov *Editors*

# Advances in Experimental and Genetic Mineralogy

Special Publication to 50th Anniversary  
of DS Korzhinskii Institute  
of Experimental Mineralogy  
of the Russian Academy of Sciences

 Springer

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of Sciences

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Dmitriy S. Korzhinskii. First Director-Organizer of the Institute of Experimental Mineralogy

# Preface



Researchers of the DS Korzhinskii Institute of Experimental Mineralogy (June 2019). *First row, from left* Vitaliy Chevychelov, Ekaterina Brichkina, Mariya Golunova, Alexey Kotelnikov, Yuriy Shapovalov, Oleg Safonov, Mikhail Zelenskiy, Anastasiya Kuzuyra, Vera Ermolaeva, Tatiana Setkova, Vladimir Balitskiy, Sergey Pivovarov. *Second row, from left* Aleksander Redkin, Yuriy Litvin, Nikolay Bezmen, Olga Shaposhnikova, Valentina Butvina, Tatiana Kovalskaya, Vera Devyatova, Anastasiya Kostyuk, Anna Spivak. *Third row, from left* Dmitriy Khanin, Konstantin Van, Valentina Korzhinskaya, Natalia Kotova, Paver Bukhtiyarov, Eduard Persikov, Kiril Shmulovich, Aleksander Simakin, Olga Karaseva. Galina Akhmedzhanova, Dmitriy Varlamov. *Back rows, from left* Galina Kashirtseva, Evgeniy Limanov, Liudmila Sipavina, Andrey Plyasunov, Natalia Suk, Nikolay Gorbachev, Evgeniy Osadchiy, Veniamin Polyakov, Pavel Gorbachev, Galina Bondarenko, Leonid Lakshtanov, Dilshad Sultanov, Tatiana Bublikova, Mikhail Voronin

This book *Advances in Experimental and Genetic Mineralogy* is devoted to 50th anniversary of the DS Korzhinskii Institute of Experimental Mineralogy of the Russian Academy of Sciences. This book has been prepared by the researchers of the institute and gives an indication of a variety of its present-day experimental and theoretical inquiries.

The Institute of Experimental Mineralogy has been organized at a period of August 1–October 1, 1969, in Chernogolovka town as a part of the Near-Moscow Scientific center of the USSR Academy of Sciences accordingly to the suggestion of academician Dmitry Sergeevich Korzhinskii who becomes the first director of the institute. D. S. Korzhinskii has made a basic contribution to working out the methods of physicochemical analyses for the metasomatic, metamorphic and magmatic processes under conditions of the Earth's crust and mantle. His pioneering investigations being directed onto the development of physicochemical methodology in studying and cognition of the basic regularities of the geologic processes date back to a beginning of the 1930s. In succeeding years, D. S. Korzhinskii and his disciples have actively developed this line of inquiry, and the results of their studies gained general recognition.

By the 1950–1960s, it dated a creation of the specialized laboratories for experimental studies of the deep-seated materials and processes under high pressure and high temperature in Moscow in the Institute of the Earth Physics (Prof. M. Volarovich), Institute of Geochemistry and Analytical Chemistry (Prof. N. Khitarov) and Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (Prof. I. Ostrovskiy) and in Novosibirsk in the Institute of Geology and Geophysics (Dr. I. Malinovskiy). At the end of 1960s, it has evolved the Laboratory of Experimental Mineralogy in the Institute of Solid State Physics (Prof. I. Ivanov) in the scientific center in Chernogolovka. Then in 1969, by the presentation of academician D. S. Korzhinskii, it has adopted a decision of reorganization of the laboratory into the Institute of Experimental Mineralogy for the fundamental experimental and theoretical studies in the fields of genetic mineralogy, physicochemical petrology and physical geochemistry. At the advent of the institute, it were taken into account the diversity and range of the magmatic, metamorphic, hydrothermal and ore-forming processes in the substance of the Earth's crust and mantle which have been going on at natural conditions over a wide range of temperature, pressure and reduction–oxidation potentials.

The disciples and colleagues of D. S. Korzhinskii become the first research workers and leaders of the scientific laboratories of the new institute. There are the well-known scientists Vilen Zharikov, Aleksey Marakushev, Leonid Perchuk, Ivan Ivanov, Georgiy Zaiskiy, Ivan Nekrasov. Their theoretical and experimental searches were of considerable importance in the making the prospective themes of scientific researches by the institute collective. In the institute, it is worked out and brought into being the unique complex of hydrothermal, gas and solid-phase apparatus of high pressure and temperature. The research activity of the institute has focused onto the experimental studies of physicochemical properties of minerals

and simplified and multicomponent mineral systems for the purpose of application of their results to the elaboration of physicochemical genetic models for the minerals, mineral assemblies and rocks, including the ore-bearing ones, at the deep-seated horizons of the Earth's crust and mantle.

The book *Advances in Experimental and Genetic Mineralogy* is originated by the scientists of the DS Korzhinskii Institute of Experimental Mineralogy (Russian Academy of Sciences) and reflects the present-day lines of experimental and theoretical studies. The book presents the fundamental experimental data and development of the experiment-based theoretical conclusions and physicochemical models for the natural hydrothermal, metasomatic, metamorphic, magmatic and ore-producing processes of the Earth's crust, upper mantle, transition zone and lower mantle. The topics discussed in the book concern the interaction of oil and aqueous fluids that is revealed by the methodology of aqueous-hydrocarbonic inclusions in synthetic quartz and applied to the natural evolution of the oil; the determination of solubility and interphase partitioning of trace and strategic elements and their components; and the experimental substantiation of physicochemical mechanisms for ultrabasic–basic evolution of the deep-mantle magmatic and diamond-forming systems. Experimental studies of physicochemical properties of supercritical water and hydrothermal fluids, viscosity of acidic ultramafic magmatic melts, peculiarities of metamorphism of basic rocks, kinetics of mineral nucleation in silicate melts and hydrothermal solutions, influence of the complex  $\text{H}_2\text{O}-\text{CO}_2-\text{HCl}$  fluids onto melting relations of the mantle–crust rocks have been marked with novel results and conclusions. The book is of interest for the Earth scientists, lecturers and students specialized in experimental and genetic mineralogy, petrology and geochemistry.

Chernogolovka, Russia

Oleg Safonov  
Yuriy Litvin

# Contents

## Part I Crystallization and Properties of Minerals and Mineral-Forming Solutions

|          |                                                                                                                                                                                                                                  |            |
|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>1</b> | <b>Phase Composition and States of Water-Hydrocarbon Fluids<br/>at Elevated and High Temperatures and Pressures<br/>(Experiment with the Use of Synthetic Fluid Inclusions) . . . . .</b>                                        | <b>3</b>   |
|          | V. S. Balitsky, T. V. Setkova, L. V. Balitskaya, T. M. Bublikova,<br>and M. A. Golunova                                                                                                                                          |            |
| <b>2</b> | <b>Experimental Studies of Hydrothermal Fluid . . . . .</b>                                                                                                                                                                      | <b>35</b>  |
|          | G. V. Bondarenko and Y. E. Gorbaty                                                                                                                                                                                               |            |
| <b>3</b> | <b>Influence of Silicate Substance on Pyrochlore and Tantalite<br/>Solubility in Fluoride Aqueous Solutions<br/>(Experimental Studies) . . . . .</b>                                                                             | <b>49</b>  |
|          | A. R. Kotelnikov, V. S. Korzhinskaya, Z. A. Kotelnikova,<br>and N. I. Suk                                                                                                                                                        |            |
| <b>4</b> | <b>Experimental and Theoretical Studies of the Viscosity of the Fluid<br/>Magmatic Systems in Conjunction with the Structure of Melts<br/>at the Thermodynamic Parameters of the Earth's Crust<br/>and Upper Mantle. . . . .</b> | <b>69</b>  |
|          | E. S. Persikov and P. G. Bukhtiyarov                                                                                                                                                                                             |            |
| <b>5</b> | <b>Crystallization of Cpx in the Ab-Di System Under the Oscillating<br/>Temperature: Contrast Dynamic Modes at Different Periods<br/>of Oscillation. . . . .</b>                                                                 | <b>97</b>  |
|          | Alexander G. Simakin, Vera N. Devyatova, and Alexey N. Nekrasov                                                                                                                                                                  |            |
| <b>6</b> | <b>Solubility and Volatility of MoO<sub>3</sub> in High-Temperature<br/>Aqueous Solutions. . . . .</b>                                                                                                                           | <b>121</b> |
|          | A. V. Plyasunov, T. P. Dadze, G. A. Kashirtseva, and M. P. Novikov                                                                                                                                                               |            |

|                                                  |                                                                                                                                                                                                               |            |
|--------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>7</b>                                         | <b>Experimental Determination of Ferberite Solubility<br/>in the KCl–HCl–H<sub>2</sub>O System at 400–500 °C and 20–100 MPa . . . .</b>                                                                       | <b>137</b> |
|                                                  | Alexander F. Redkin and Gary L. Cygan                                                                                                                                                                         |            |
| <br><b>Part II Genesis of Minerals and Rocks</b> |                                                                                                                                                                                                               |            |
| <b>8</b>                                         | <b>Evolution of Mantle Magmatism and Formation<br/>of the Ultrabasic-Basic Rock Series: Importance of Peritectic<br/>Reactions of the Rock-Forming Minerals . . . . .</b>                                     | <b>165</b> |
|                                                  | Yu. A. Litvin, A. V. Kuzyura, and A. V. Spivak                                                                                                                                                                |            |
| <b>9</b>                                         | <b>Formation of K–Cr Titanates from Reactions of Chromite<br/>and Ilmenite/Rutile with Potassic Aqueous-Carbonic Fluid:<br/>Experiment at 5 GPa and Applications to the Mantle<br/>Metasomatism . . . . .</b> | <b>201</b> |
|                                                  | V. G. Butvina, S. S. Vorobey, O. G. Safonov, and G. V. Bondarenko                                                                                                                                             |            |
| <b>10</b>                                        | <b>How Biopolymers Control the Kinetics of Calcite Precipitation<br/>from Aqueous Solutions . . . . .</b>                                                                                                     | <b>223</b> |
|                                                  | L. Z. Lakshtanov, O. N. Karaseva, D. V. Okhrimenko,<br>and S. L. S. Stipp                                                                                                                                     |            |
| <b>11</b>                                        | <b>The Evolutionary Types of Magmatic Complexes<br/>and Experimental Modeling Differentiation Trends . . . . .</b>                                                                                            | <b>247</b> |
|                                                  | N. I. Bezmen and P. N. Gorbachev                                                                                                                                                                              |            |
| <b>12</b>                                        | <b>Influence of C–O–H–Cl-Fluids on Melting Phase Relations<br/>of the System Peridotite-Basalt: Experiments at 4.0 GPa . . . . .</b>                                                                          | <b>271</b> |
|                                                  | N. S. Gorbachev, A. V. Kostyuk, P. N. Gorbachev, A. N. Nekrasov,<br>and D. M. Soultanov                                                                                                                       |            |
| <b>13</b>                                        | <b>Inter-phase Partitioning of Pb and Zn in Granitoid<br/>Fluid-Magmatic Systems: Experimental Study . . . . .</b>                                                                                            | <b>289</b> |
|                                                  | V. Yu. Chevychelov                                                                                                                                                                                            |            |
| <b>14</b>                                        | <b>Experimental Study of Amphibolization of the Basic Rocks<br/>of the Tiksheozersky Massif . . . . .</b>                                                                                                     | <b>337</b> |
|                                                  | T. N. Kovalskaya, D. A. Varlamov, Y. B. Shapovalov, G. M. Kalinin,<br>and A. R. Kotelnikov                                                                                                                    |            |

# Abbreviations

|             |                                                                                                                                                            |
|-------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Ab          | Albite $\text{NaAlSi}_3\text{O}_8$                                                                                                                         |
| Alm         | Almandine $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$                                                                                                 |
| An          | Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$                                                                                                             |
| Ancl        | Anorthoclase $(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$                                                                                                |
| And         | Andalusite $\text{Al}_2\text{SiO}_5$                                                                                                                       |
| Brd         | Bridgmanite $\text{MgSiO}_3$                                                                                                                               |
| CaPrv       | Ca-perovskite $\text{CaSiO}_3$                                                                                                                             |
| Carb, Carb* | Assembly of several carbonates                                                                                                                             |
| Chr         | Chromite $\text{FeCr}_2\text{O}_4$                                                                                                                         |
| Coe         | Coesite $\text{SiO}_2$                                                                                                                                     |
| Cpx         | Clinopyroxene $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe})(\text{Si}, \text{Al})_2\text{O}_6$ ; $[(\text{Di}\cdot\text{Hd}\cdot\text{Jd})_{\text{ss}}]$   |
| Crn         | Corundum $\text{Al}_2\text{O}_3$                                                                                                                           |
| D           | Diamond C                                                                                                                                                  |
| Di          | Diopside $\text{CaMgSi}_2\text{O}_6$                                                                                                                       |
| Dol         | Dolomite $\text{CaMg}(\text{CO}_3)_2$                                                                                                                      |
| En          | Enstatite $\text{MgSiO}_3$                                                                                                                                 |
| Fa          | Fayalite $\text{Fe}_2\text{SiO}_4$                                                                                                                         |
| FBrd        | Ferrobridgmanite $(\text{Mg}, \text{Fe})\text{SiO}_3$                                                                                                      |
| Fo          | Forsterite $\text{Mg}_2\text{SiO}_4$                                                                                                                       |
| FPer        | Ferropericlase $(\text{Mg}, \text{Fe})\text{O}$                                                                                                            |
| FRwd        | Ferroringwoodite $(\text{Mg}, \text{Fe})_2\text{SiO}_4$                                                                                                    |
| Fs          | Ferrosilite $\text{FeSiO}_3$                                                                                                                               |
| Gros        | Grossularite $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$                                                                                              |
| Grt         | Garnet $(\text{Mg}, \text{Fe}, \text{Ca})_3(\text{Al}, \text{Cr})_2\text{Si}_3\text{O}_{12}$ ; $[(\text{Prp}\cdot\text{Alm}\cdot\text{Gros})_{\text{ss}}]$ |
| Hd          | Hedenbergite $\text{CaFeSi}_2\text{O}_6$                                                                                                                   |
| Jd          | Jadeite $\text{NaAlSi}_2\text{O}_6$                                                                                                                        |
| Kfs         | K-feldspar $\text{KAlSi}_3\text{O}_8$                                                                                                                      |
| Ky          | Kyanite $\text{Al}_2\text{SiO}_5$                                                                                                                          |
| L           | Liquid, melt                                                                                                                                               |
| Ma          | Mathiasite $(\text{K}, \text{Ba}, \text{Sr})(\text{Zr}, \text{Fe})(\text{Mg}, \text{Fe})_2(\text{Ti}, \text{Cr}, \text{Fe})_{18}\text{O}_{38}$             |

|      |                                                                                                                                        |
|------|----------------------------------------------------------------------------------------------------------------------------------------|
| Mcl  | Microlite $\text{NaCaTa}_2\text{O}_6\text{F}$                                                                                          |
| Mgs  | Magnesite $\text{MgCO}_3$                                                                                                              |
| Mic  | Microcline $\text{KAlSi}_3\text{O}_8$                                                                                                  |
| MWus | Magnesiowustite $(\text{Fe}, \text{Mg})\text{O}$                                                                                       |
| Ol   | Olivine $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ ; $[(\text{Fo}\cdot\text{Fa})_{\text{ss}}]$                                             |
| Olg  | Oligoclase $(\text{Na}, \text{Ca})(\text{Si}, \text{Al})_4\text{O}_8$                                                                  |
| Omph | Omphacite, Jd-rich clinopyroxene                                                                                                       |
| Opx  | Orthopyroxene $(\text{Mg}, \text{Fe})\text{SiO}_3$ ; $[(\text{En}\cdot\text{Fs})_{\text{ss}}]$                                         |
| Par  | Paragonite $\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$                                                                        |
| Pchl | Pyrochlore $(\text{Ca}, \text{Na})_2(\text{Nb}, \text{Ta})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$                                 |
| Per  | Periclase $\text{MgO}$                                                                                                                 |
| Pf   | Pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$                                                                        |
| Phl  | Phlogopite $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$                                                             |
| Pl   | Plagioclase $(\text{NaAlSi}_3\text{O}_8\cdot\text{CaAl}_2\text{Si}_2\text{O}_8)_{\text{ss}}$ ; $(\text{Ab}\cdot\text{An})_{\text{ss}}$ |
| Pri  | Priderite $(\text{K}, \text{Ba})(\text{Ti}, \text{Fe}, \text{Mn})_8\text{O}_{16}$                                                      |
| Prp  | Pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$                                                                                |
| Qz   | Quartz $\text{SiO}_2$                                                                                                                  |
| Rwd  | Ringwoodite $\text{Mg}_2\text{SiO}_4$                                                                                                  |
| Srp  | Serpentine $(\text{Mg}, \text{Fe}, \text{Ni}, \text{Al}, \text{Zn}, \text{Mn})_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4$                |
| Sti  | Stishovite $\text{SiO}_2$                                                                                                              |
| Tnt  | Tantalite $(\text{Mn}, \text{Fe})(\text{Nb}, \text{Ta})_2\text{O}_6$                                                                   |
| Wds  | Wadsleyite $\text{Mg}_2\text{SiO}_4$                                                                                                   |
| Wol  | Wollastonite $\text{CaSiO}_3$                                                                                                          |
| Wus  | Wustite $\text{FeO}$                                                                                                                   |
| Yim  | Yimendite $\text{K}(\text{Cr}, \text{Ti}, \text{Mg}, \text{Fe}, \text{Al})_{12}\text{O}_{19}$                                          |

## Physical Symbols

|                      |                                                                              |
|----------------------|------------------------------------------------------------------------------|
| $A_{Kr}$             | The Krichevskii parameter                                                    |
| $f_1^*$              | The pure water fugacity                                                      |
| $f_2$                | The fugacity of a solute                                                     |
| $G^o(g)$             | The Gibbs energy of a compound in the ideal gas state                        |
| $G_2^\infty$         | The Gibbs energy of a compound in the state of the standard aqueous solution |
| $K_D$                | The vapor–liquid distribution constant                                       |
| $k_H$                | Henry's constant                                                             |
| $m$                  | Molality (a number of moles of a substance in 1000 g of water)               |
| $N_w \approx 55.508$ | The number of moles of $\text{H}_2\text{O}$ in 1 kg of water                 |
| $P_1^*$              | Pressure of saturated water vapor                                            |
| $T_c$                | The critical temperature of pure water                                       |

## Greek Symbols

|                 |                                                                                   |
|-----------------|-----------------------------------------------------------------------------------|
| $\rho_c$        | The critical density of pure water                                                |
| $\rho_1^*(L)$   | The pure water density along the liquid side of the saturation vapor–liquid curve |
| $\phi_1^*$      | The fugacity coefficient of pure water                                            |
| $\phi_2^\infty$ | The fugacity coefficient of a solute at infinite dilution in water                |

**Part I**  
**Crystallization and Properties**  
**of Minerals and Mineral-Forming**  
**Solutions**

## Chapter 7

# Experimental Determination of Ferberite Solubility in the KCl–HCl–H<sub>2</sub>O System at 400–500 °C and 20–100 MPa



Alexander F. Redkin and Gary L. Cygan

**Abstract** The solubility of ferberite, FeWO<sub>4</sub> was studied at 400–500 °C, pressures of 20, 25, 40, 50 and 100 MPa, oxygen fugacity corresponding to the Ni–NiO, Fe<sub>3</sub>O<sub>4</sub>–Fe<sub>2</sub>O<sub>3</sub> buffers, in 0.7 ÷ 8.9 *m*KCl solutions and acidity controlled by quartz–microcline–muscovite buffer assemblage. The parameters of the experiments cover both the field of homogeneous solutions and the region of immiscibility in the KCl–H<sub>2</sub>O system. The total W concentration depends upon *m*Cl, *T* and *f*O<sub>2</sub> in the system and range from 1 · 10<sup>–4</sup>–0.05 mol kg<sup>–1</sup> in 0.7 *m*KCl to 0.01–0.15 in 8.9 *m*KCl. The results suggest a large bulk solubility in the dense, salt-rich phase of the two-phase fluid. Ferberite dissolution in KCl solutions under pH and *f*O<sub>2</sub> buffered conditions at 400–500 °C proceeds congruently as well as incongruently with accompanying potassium tungsten bronzes formation, K<sub>x</sub>WO<sub>3</sub>, (*x* = 0.2–0.3). Thermodynamic calculations performed for a homogeneous solution at *P* = 100 MPa indicate that the predominant aqueous species of tungsten in KCl–HCl solutions at *f*O<sub>2</sub> = *f*O<sub>2</sub>(Ni–NiO) may be W(V, VI) species: WO<sub>3</sub><sup>–</sup>, HWO<sub>4</sub><sup>–</sup>, H<sub>2</sub>W<sub>2</sub>O<sub>7</sub><sup>–</sup> at 500 °C and HWO<sub>4</sub><sup>–</sup>, W<sub>5</sub>O<sub>16</sub><sup>3–</sup> at 400 °C. Application of the extended FeWO<sub>4</sub> solubility model to natural systems suggest that deposition of tungsten from ore-bearing solutions is due to interaction with wall rocks containing feldspars, and iron oxides together with decreasing temperatures. In the magnetite bearing system, the equilibrium tungsten concentration does not exceed 2 · 10<sup>–5</sup> mol kg<sup>–1</sup> at temperatures of 400 °C.

**Keywords** Ferberite · Potassium tungstate bronze · Solubility · Buffered system · Homogenous solution · Immiscibility region · Tungsten species

## 7.1 Introduction

Wolframite, (Fe, Mn)<sup>+2</sup>WO<sub>4</sub>, as well as its end members ferberite, FeWO<sub>4</sub>, and huebnerite, MnWO<sub>4</sub>, are the main ore minerals associated with hydrothermal deposits of

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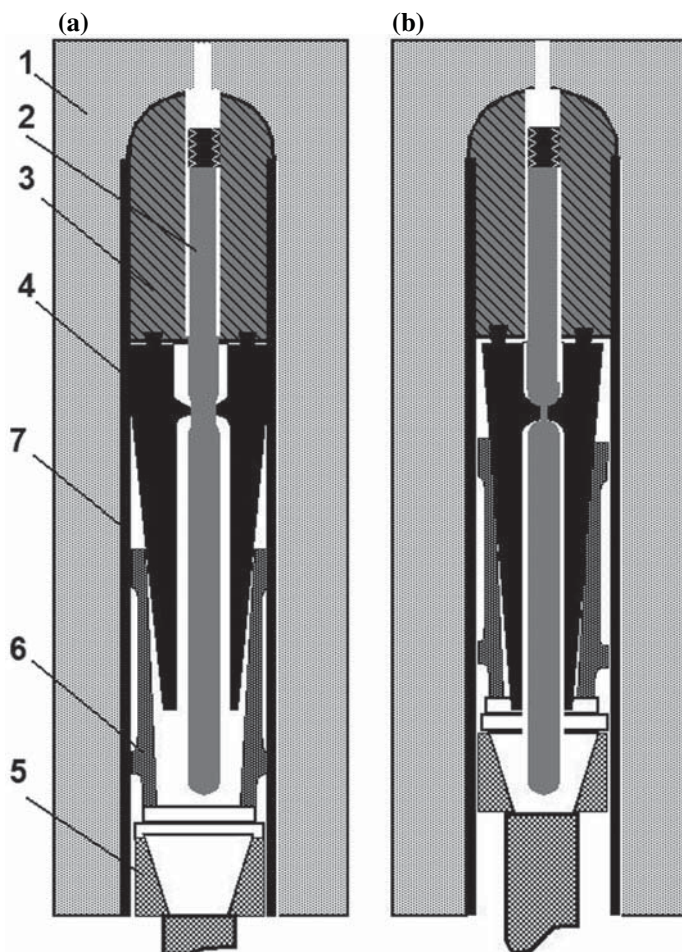
137

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tungsten related to the metasomatic processes of granite greisenization and albitization. Tungsten ore deposition usually occurs late in the paragenetic sequence and is typically located in the apical segments of massifs. Mineralization typically occurs at depths equated with the range of 100–150 m. Temperature conditions of ore formation are estimated to be in the interval 300–540 °C (Smirnov et al. 1981). According to mineral-geochemical investigations ore deposition took place in several stages, typically as part of the post-greisen stage of development. The greisen metasomatic process created conditions appropriate for leaching W and other ore elements (e.g., Fe, U, REE) from the surrounding rocks interacting with the hydrothermal solutions. The analysis of gas-liquid inclusions in quartz from greisen of different generations (Ivanova et al. 1986) indicate wolframite deposits were formed under the influence of solutions containing high concentrations of salts (dominantly NaCl, KCl), carbon dioxide and rich in fluorides. Hydrothermal solutions containing tungsten leached iron from the host rock, effectively bleaching the host rock. It appears that the calcium content in these hydrothermal solutions is not critical since we observe sheelite ( $\text{CaWO}_4$ ) mineralization principally associated with skarns. Tungsten ore deposition in these, high-temperature, high-concentration salt solutions occurred during the greisen stage of the hydrothermal process. The hydrothermal solution had the same acidity as that of the solutions forming quartz-topaz and quartz-mica (muscovite) greisens. For these reasons, a study of ferberite solubility in highly concentrated salt solutions, particularly the two-phase region of aqueous-salt fluids, under buffered conditions is a principal problem in tungsten geochemistry. In addition, investigations into the effect of pressure on the solubility of ore minerals is also of considerable interest since it has been demonstrated by Hemley et al. (1986, 1992), Malinin and Kurovskaya (1996) that pressure decreases can increase metal solubility in acid-buffered systems.

## 7.2 Experimental Procedures

Experiments were performed at 400–500 °C and pressures of 20, 25, 40, 50 and 100 MPa using large volume hydrothermal pressure vessels (30 mm internal diameter  $\times$  200 mm long): cold-seal pressure vessels (Tuttle bombs) and a pinch-off vessel (Ivanov et al. 1994). A drawing of the Pinch-off device in thin-wall capsule of gems is represented in Fig. 7.1a, b. The experimental charge in the welded capsule is positioned in the clamping mechanism and placed between the two halves of the prop above the connector. The clamp location on the capsule may be moved so that the ratio of the separated, or “pinched-off” capsule may be varied (Fig. 7.1a). This pinch-off mechanism is operated by way of a hydraulic push of the rod that moves the pinching tool upwards causing the pinching effect to occur. The pincer consists of two identical halves with a conical external surface, specially designed internal longitudinal hollows and transverse connectors. Crushing and collapsing of the capsule does not occur because of these longitudinal grooves and connectors. The walls of the capsule are pressed tightly enough that a weld occurs at the pinch point



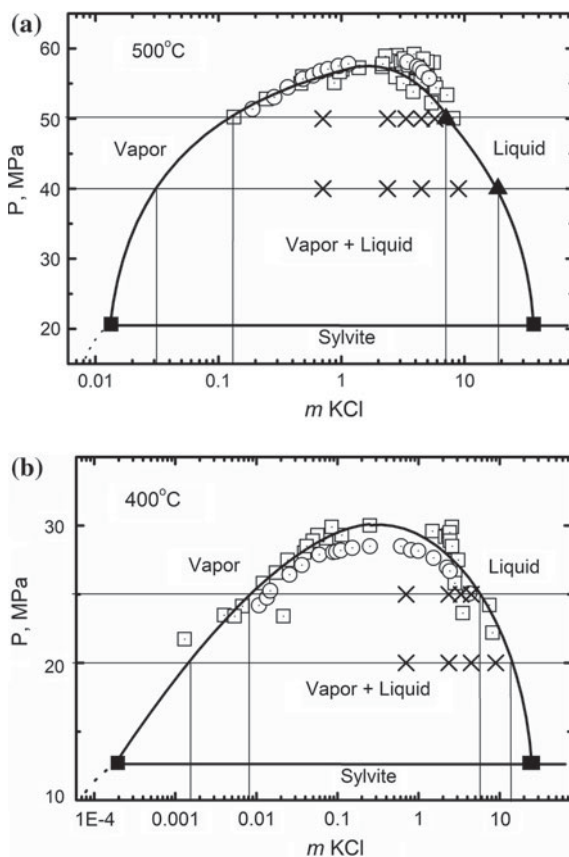
**Fig. 7.1** Schematic showing the pinch-off vessel used for separation of media under hydrothermal conditions: **a** initial state; **b** after the separator with the one connector has been activated. Details of the device: 1—Ni-alloy reactor, 2—capsule, 3—stop holder (two details), 4—separator or capsule clamp (two details), 5—movable socket rod, 6—movable sleeve, 7—tube

(Fig. 7.1b). The hot spot of the furnace was measured and found to have a thermal gradient of 2–3 °C over 12 cm. The capsule pinching was done after the necessary time required for establishing equilibrium. The pinch-off vessel was used to refine KCl concentration in brine at 500 °C and pressure of 40 and 50 MPa.

Using large volume vessel (cold seals Tuttle bomb), four experiments on ferberite solubility were run simultaneously. Temperature was regulated using a high-precision controller using chromel–alumel thermocouples between the experimental capsules. The thermocouple uncertainty is  $\pm 2\text{--}3$  °C. Experiments at pressures of 20–50 MPa were set using a Burdon manometer for pressures of up to 60 MPa and an uncertainty

of  $\pm 0.2$  MPa. Experiments conducted at 100 MPa used a 2500-style manometer with an accuracy of  $\pm 15$  MPa. Experimental run times were from 14 to 30 days, depending upon  $P$  and  $T$ , though previous studies in similar systems containing the ore minerals  $\text{SnO}_2$ ,  $\text{UO}_2$ ,  $\text{CaWO}_4$ , indicate equilibrium with the solutions is approached in several hours to less than 7 days (Dadze et al. 1981; Kovalenko et al. 1986; Redkin et al. 1989; Malinin and Kurovskaya 1996).

Study of ferberite solubility in aqueous-salt KCl–HCl solutions was made in platinum capsules, 60–90 mm long  $\times$  7–8 mm diameter. The starting solutions for the experiments were made from commercial reagents of high-purity KCl, HCl and doubly-distilled water. Pressures and starting KCl compositions were chosen such that the experiments would be in the two-phase region (Fig. 7.2a, b). At 500 °C and



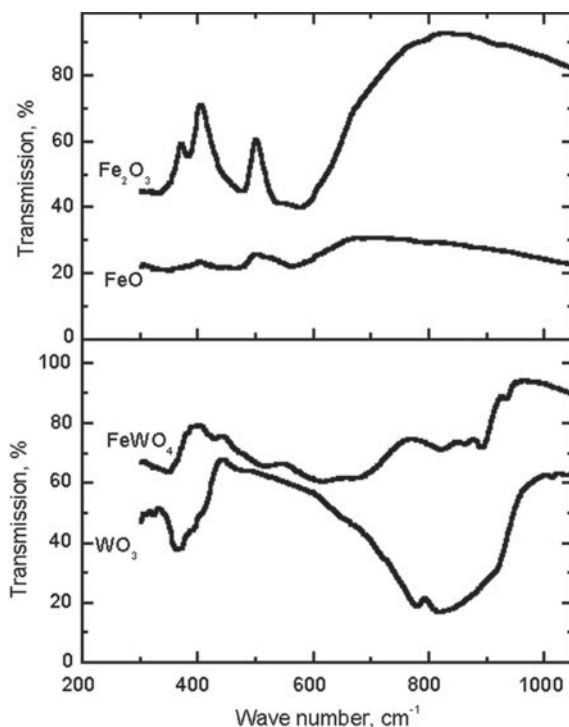
**Fig. 7.2** Vapor and liquid compositions along the 500 (a) and 400 °C (b) isothermal coexistence curves for the KCl–H<sub>2</sub>O system. Solid square symbols for three-phase (sylvite-liquid-vapor) by Hovey et al. (1990). For two-phase region: dotted square by Cygan et al. (1994), dotted round by Shmulovich et al. (1995), solid triangles represent our data obtained using the pinch-off device. The initial  $m$ KCl values used in the runs on ferberite solubility are shown by “X”

a pressure of 40 and 50 MPa, 5, 15, 25 and 20 or 30 wt% solutions of KCl were used (Fig. 7.2a), and at 400 °C 20, 25 and 100 MPa, 5, 15, 25 and 40 wt% of KCl were used (Fig. 7.2b). The initial solutions also contained HCl of 0.01 and 0.1 or 0.001 mol/kg H<sub>2</sub>O. Varying starting  $m\text{KCl}/m\text{HCl}$  ratios made it possible to approach equilibrium in the QMM buffer system from both sides as was done by Hemley (1959).

Ferberite starting material was synthesized through recrystallization of a mixture of FeO and WO<sub>3</sub> in a solution of 30 wt% LiCl in gold capsules. The ratio of the aqueous solution to the solid mixture was about 2:1 by weight. This mixture was then reacted at 500 °C and 100 MPa (Klevtsov et al. 1970) for 14 days. This produced grain sizes of 5–10 µm in diameter, and subsequent recrystallization in the same solution and  $T$  at  $P = 40$  MPa for 14 days yielded grains diameters of 15–25 µm. X-ray diffraction scans of synthetic ferberite correspond to the standard sample 27–256 (PDF 1980), while microprobe analyses indicate the composition corresponds to the stoichiometric formula of ferberite, FeWO<sub>4</sub>. Fourier transform infrared (FTIR) spectrum of the synthetic ferberite, depicted in Fig. 7.3, also indicates that the synthesized product is pure and complete conversion of FeO and WO<sub>3</sub> has occurred.

The initial solid charge consisted of a mixture of 20 mg of ferberite with 60 mg of the alumina-silicate buffer, quartz (SiO<sub>2</sub>)-microcline (KAlSi<sub>3</sub>O<sub>8</sub>)-muscovite (KAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>)-(QMM). The initial Na<sub>2</sub>O concentration of a natural pegmatitic

**Fig. 7.3** Infra-red spectra of synthetic ferberite and the starting compounds FeO and WO<sub>3</sub> used in the ferberite synthesis



microcline (as Mic phase) was decreased through exposure to molten KCl. The exchange yielded a microcline composition of (in wt%) SiO<sub>2</sub>-65.59, Al<sub>2</sub>O<sub>3</sub>-17.72, K<sub>2</sub>O-16.44, FeO < 0.12, TiO<sub>2</sub> < 0.06, Na<sub>2</sub>O, MnO, MgO, Cr<sub>2</sub>O<sub>3</sub>, CaO < 0.02. Pegmatic 2M<sub>1</sub> muscovite was processed by rubbing plates of the pure natural mineral (composition (in wt%) SiO<sub>2</sub>-47.79, TiO<sub>2</sub>-0.64, Al<sub>2</sub>O<sub>3</sub>-32.46, Fe<sub>2</sub>O<sub>3</sub>-3.17, MnO-0.13, MgO-1.317, CaO-0.070, Na<sub>2</sub>O-0.61, K<sub>2</sub>O-10.77, H<sub>2</sub>O + 2.52, F<sub>2</sub> < 0.04). The muscovite was sieved to 20–300 µm and then purified in dilute HCl. Before crushing in an agate mortar, synthetic quartz was heated briefly in a furnace to 700 °C and quenched in pure water to form fractures. The QMM buffer is required in this study to provide a constant KCl/HCl ratio in the aqueous phase to control the system's acidity through the following reaction:



In the two-phase region of the KCl–H<sub>2</sub>O system, the QMM buffer will provide constant concentrations of KCl and HCl in each phase at a given *T* and *P*. A change in the initial KCl concentration alters the relative masses or volumes of the L and V phases, but not the KCl and HCl concentrations (Cygan et al. 1994).

Oxygen fugacity in the experiments was controlled using the nickel-bunsenite (NNO,  $f_{\text{O}_2} = 10^{-17.70}$  at 500 °C and  $10^{-22.42}$  Pa at 400 °C) and hematite-magnetite oxygen buffers (HM,  $f_{\text{O}_2} = 10^{-13.63}$  Pa at 500 °C). The buffers consisted of approximately a 1:1 ratio of fine-crystalline metallic nickel and bunsenite or synthetic magnetite and commercial hematite, a total amount of 3–4 g was placed into the Ni-alloy container. The presence of Ni and Fe<sub>3</sub>O<sub>4</sub> in the reaction mixture after the runs was checked by magnet.

Platinum capsules with the charge of solid phases (80 mg) and solution (0.4 ml) were assembled. The air above the charge was removed by blowing pure argon through the capsule before welding. We feel this contributed to a more rapid attainment of equilibrium  $f_{\text{O}_2}$ .

The charges were quenched to room temperature using an air-water mixture for 7–10 min. The capsules were recovered, dried and weighed to check for the integrity of the capsule seal. Capsules showing less than ±5 mg change in weight were considered valid runs. The capsules were opened and the solutions and the charge were washed into plastic test-tubes using approximately a 20-fold volume of doubly-distilled water. The dilution of the recovered aqueous solution was determined by weighing the washed material to an accuracy of ±0.03 mg. These solutions were then centrifuged at a velocity of 5000–6000 rpm for 2–3 min. An aliquot of pure solution for chemical analysis was removed. The recovered solid materials were washed with doubly-distilled water and then centrifuged and dried in ceramic cups at 100–120 °C.

The transparent, colorless solutions were subjected to spectrophotometric analysis for tungsten using a Spekol-11 (Germany) and the bromopyrogallol red technique (Andreeva et al. 1992). For iron we used the ortho-phenantroline and α, α-dipyridill technique (Marczenko 1976), and for SiO<sub>2</sub>, mainly the molybdate yellow method (Teleshova 1973). Aqueous Al analyses were performed using an atomic absorption

spectrometer (Perkin-Elmer model 403). All our attempts to use spectrophotometric analysis for Al using the antrazochrom technique (Basargin et al. 1976) were unsuccessful due to the strong interfering effect that high W concentrations had on measurements. The analytical error for Fe is estimated to be <5%, for W and SiO<sub>2</sub> < 10%, and for Al < 30%. Solid charge products were subjected to a quantitative microprobe analysis using a Camebax MBX at E<sub>0</sub> = 15 keV, the size of beam of electrons Ø = 1–2 µm and X-ray diffraction investigations using a DRON-2 (made in Russia) with Cu-Kα.

### 7.3 Solubility-Salt Concentration Correlation

The solubility of a congruently-dissolving mineral in the two-phase region at constant pressure and acidity of the V and L phases can be described by the equation

$$S_{\text{total}} = S^V \cdot X_V + S^L \cdot X_L = S^V + X_L \cdot (S^L - S^V), \quad (7.2)$$

where  $S_{\text{total}}$  is a total mineral solubility in the two-phase region (wt%),  $S^L$  and  $S^V$  are the mineral solubility in L (high-density) and V (low-density) phases, and  $X_L$  and  $X_V$  are the mass fractions of L and V. Equation (7.2) represents a general expression of the lever rule for phases in equilibrium, and describes the distribution of KCl as well

$$C_{\text{salt}}^T = C_{\text{salt}}^L \cdot X_L + C_{\text{salt}}^V \cdot X_V,$$

where  $C_{\text{salt}}^T$ ,  $C_{\text{salt}}^L$ , and  $C_{\text{salt}}^V$  are the total concentration of salt and concentrations of salt in the coexisting L and V phases in wt%, respectively. It follows,

$$X_L = (C_{\text{salt}}^T - C_{\text{salt}}^V) / (C_{\text{salt}}^L - C_{\text{salt}}^V). \quad (7.3)$$

Replacing  $X_L$  in (7.2) by (7.3) we get the expression where mineral solubility depends linearly on total salt concentration,  $C_{\text{salt}}^T$ , whereas  $S^V$ ,  $S^L$ ,  $C_{\text{salt}}^L$ , and  $C_{\text{salt}}^V$  are constant:

$$S_{\text{total}} = S^V + (S^L - S^V) \cdot (C_{\text{salt}}^T - C_{\text{salt}}^V) / (C_{\text{salt}}^L - C_{\text{salt}}^V), \quad (7.4)$$

and  $S_{\text{total}} = S^V$  at  $C_{\text{salt}}^T = C_{\text{salt}}^V$  and  $S_{\text{total}} = S^L$  at  $C_{\text{salt}}^T = C_{\text{salt}}^L$ . It is clear that in the two-phase region, we can speak about solubility of a compound either in a liquid or in the vapor phase. However, the value  $S_{\text{total}}$  itself represents an apparent solubility, that is, a total solubility obtained after fluid homogenization after quench. Nevertheless, these apparent mineral solubility data may be described by using a linear function of the total salt concentration in a fluid.

## 7.4 Results and Discussions

### 7.4.1 Solutions After the Runs

Experimental results are represented in Table 7.1 and Fig. 7.4a, b. Quench pH values of parallel experiments, that is, experiments made at the same initial concentration of KCl but different  $m\text{HCl}$  (0.1 and 0.01), are quite similar indicating the acidic-alkaline equilibrium between the QMM buffer and KCl–HCl–H<sub>2</sub>O solution is operating. The divergence in  $m\text{HCl}$  values of some runs, especially those conducted in 40 wt% KCl starting solutions (Fig. 7.5), may be related to the effect of high concentrations of Fe and W on the quenched pH value ( $m\text{HCl}$ ). Total W and Fe concentrations are a function of the  $m\text{KCl}$  and the initial  $m\text{HCl}$ . These varied from  $1 \cdot 10^{-4}$ –0.05 in 0.7  $m\text{KCl}$  starting solution experiments to 0.01–0.15 m in 8.9  $m\text{KCl}$  (see Fig. 7.4a). Incongruent dissolution of ferberite is indicated by the fact that  $m\text{W}$  was consistently not equal to  $m\text{Fe}$  in the analyzed solutions. Despite the significant concentrations of W and Fe (0.02–0.15 mol kg<sup>-1</sup>) the quenched solutions were acidic, transparent, and colorless (or light blue (Busev et al. 1976)) suggesting that iron in the solutions was present as species of Fe(II). During preparation for analysis, mixing the sample with NaOH caused the formation of very small needle-like crystals of Na, K blue oxichlorwolframites(V) which then easily redissolved into the solution.

Ferberite dissolution took place in solutions saturated with QMM buffer components. Concentration of Al in these solutions was in the range of 0.0003–0.003 mol kg<sup>-1</sup>, i.e., considerably lower than the W and Fe molality. In the homogeneous, single-phase region of the KCl–HCl system, quartz solubility did not change in experiments with  $m\text{KCl}$  ranging from 0.038 to 2.367. However, quartz solubility decreased reaching 0.022  $m\text{SiO}_2$  at 500 °C (Fig. 7.6a) and 0.02  $m\text{SiO}_2$  at 400 °C in 8.942  $m\text{KCl}$  (Fig. 7.6b) experiments. Taking into account such an inadequate character of behavior of SiO<sub>2</sub> and W one can assume that in weakly-acidic concentrated aqueous-salt solutions at 500 °C and NNO buffer a formation of the marked numbers of predominant Si–W heteropolycomplexes did not take place. However, these complexes could be formed when we analyzed quenched solutions for SiO<sub>2</sub> using the blue method (Marczenko 1976) affecting the results to lower  $m\text{SiO}_2$ .

### 7.4.2 Solid Phases After the Runs

X-ray diffraction and microprobe analysis of the recovered solid phases after the experiments showed that the initial components of the QMM buffer, i.e., Mic, Ms and Qtz, did not undergo phase changes and all three minerals were present in the run products. No new alumina-silicate phases were found, and the compositions of Mic and Ms remained unchanged.

**Table 7.1** Experimental results for ferberite  $\text{FeWO}_4$  solubility in KCl–HCl solutions at QMM buffers

| $P$ (MPa)          | Time (days) | Initial solution (mol kg <sup>-1</sup> ) |       | Final solution (log $m$ ) |        |        |                  |      |
|--------------------|-------------|------------------------------------------|-------|---------------------------|--------|--------|------------------|------|
|                    |             | KCl                                      | HCl   | W                         | Fe     | Al     | SiO <sub>2</sub> | HCl* |
| 1                  | 2           | 3                                        | 4     | 5                         | 6      | 7      | 8                | 9    |
| <i>500 °C, NNO</i> |             |                                          |       |                           |        |        |                  |      |
| 100                | 18          | 0.706                                    | 0.10  | −2.234                    | −1.970 | <−3.5  | −1.468           | −1.9 |
| 100                | 22          | 0.706                                    | 0.01  | −1.941                    | −2.654 | <−3.4  | −1.457           | −2.1 |
| 100                | 18          | 2.367                                    | 0.10  | −1.787                    | −1.272 | <−3.5  | −1.414           | −1.9 |
| 100                | 22          | 2.367                                    | 0.01  | −1.691                    | −1.487 | <−3.4  | −1.430           | −1.9 |
| 100                | 18          | 4.471                                    | 0.10  | −1.680                    | −0.980 | <−3.5  | −1.455           | −1.9 |
| 100                | 22          | 4.471                                    | 0.01  | −1.380                    | −1.121 | <−3.1  | −1.493           | −2.2 |
| 100                | 18          | 8.942                                    | 0.10  | −1.683                    | −0.812 | <−3.5  | −1.704           | −3.7 |
| 100                | 22          | 8.942                                    | 0.01  | −1.260                    | −1.045 | <−3.4  | −1.613           | −3.6 |
| 50                 | 25          | 0.706                                    | 0.10  | −2.712                    | −1.355 | −3.0   | −1.782           | −1.2 |
| 50                 | 27          | 0.706                                    | 0.01  | −2.800                    | −1.642 | −3.1   | −1.835           | −1.2 |
| 50                 | 25          | 2.367                                    | 0.10  | −2.146                    | −1.022 | −2.9   | −1.599           | −1.0 |
| 50                 | 27          | 2.367                                    | 0.01  | −1.655                    | −1.250 | −3.2   | −1.661           | −1.4 |
| 50                 | 25          | 3.353                                    | 0.10  | −1.995                    | −0.914 | −3.2   | −1.557           | −1.3 |
| 50                 | 27          | 4.471                                    | 0.01  | −1.181                    | −1.073 | −3.2   | −1.556           | −1.7 |
| 50                 | 25          | 4.471                                    | 0.10  | −1.778                    | −0.882 | −3.0   | −1.523           | −1.5 |
| 50                 | 27          | 5.749                                    | 0.01  | −1.173                    | −1.101 | −3.2   | −1.512           | −2.2 |
| 40                 | 40          | 0.706                                    | 0.10  | −2.536                    | −1.224 | −2.5   | −1.724           | −1.0 |
| 40                 | 28          | 0.706                                    | 0.01  | −2.459                    | −1.352 | −2.5   | −1.745           | −0.9 |
| 40                 | 40          | 2.367                                    | 0.10  | −2.152                    | −0.991 | −3.1   | −1.852           | −1.3 |
| 40                 | 28          | 2.367                                    | 0.01  | −1.840                    | −1.147 | −3.0   | −1.816           | −1.4 |
| 40                 | 40          | 4.471                                    | 0.10  | −1.692                    | −0.887 | −3.2   | −1.883           | −1.4 |
| 40                 | 28          | 4.471                                    | 0.01  | −1.419                    | −1.061 | −3.0   | −1.914           | −1.7 |
| 40                 | 40          | 8.942                                    | 0.10  | −1.177                    | −0.888 | −3.3   | −2.009           | −2.4 |
| 40                 | 28          | 8.942                                    | 0.01  | −0.988                    | −0.983 | −3.3   | −1.786           | −3.3 |
| <i>500 °C, HM</i>  |             |                                          |       |                           |        |        |                  |      |
| 100                | 18          | 0.706                                    | 0.01  | −2.911                    | −2.017 | −1.574 | n.a.             | −1.9 |
| 100                | 22          | 0.706                                    | 0.001 | −2.505                    | −1.934 | −1.603 | n.a.             | −1.9 |
| 100                | 18          | 2.367                                    | 0.01  | −2.287                    | −1.540 | −1.688 | n.a.             | −1.7 |
| 100                | 22          | 2.367                                    | 0.001 | −1.965                    | −1.456 | −1.496 | n.a.             | −1.9 |
| 100                | 18          | 4.471                                    | 0.01  | −2.284                    | −1.437 | −1.697 | n.a.             | −2.7 |
| 100                | 22          | 4.471                                    | 0.001 | −1.744                    | −1.355 | −1.692 | n.a.             | −3.0 |
| 100                | 18          | 8.942                                    | 0.01  | −2.202                    | −1.465 | −1.986 | n.a.             | −3.7 |

(continued)

**Table 7.1** (continued)

| <i>P</i> (MPa) | Time (days) | Initial solution (mol kg <sup>-1</sup> ) |       | Final solution (log <i>m</i> ) |        |        |                  |      |
|----------------|-------------|------------------------------------------|-------|--------------------------------|--------|--------|------------------|------|
|                |             | KCl                                      | HCl   | W                              | Fe     | Al     | SiO <sub>2</sub> | HCl* |
| 1              | 2           | 3                                        | 4     | 5                              | 6      | 7      | 8                | 9    |
| 100            | 22          | 8.942                                    | 0.001 | −1.915                         | −1.383 | −2.062 | n.a.             | −3.9 |
| 50             | 25          | 0.706                                    | 0.01  | <−4.1                          | −1.646 | −1.750 | n.a.             | −1.8 |
| 50             | 27          | 0.706                                    | 0.001 | −2.584                         | −1.792 | −      | n.a.             | −1.5 |
| 50             | 25          | 2.367                                    | 0.01  | −2.067                         | −1.455 | −1.688 | n.a.             | −1.9 |
| 50             | 27          | 2.367                                    | 0.001 | −1.882                         | −1.692 | −      | n.a.             | −1.6 |
| 50             | 25          | 4.471                                    | 0.01  | −1.742                         | −1.306 | −1.556 | n.a.             | −2.7 |
| 50             | 27          | 4.471                                    | 0.001 | −1.713                         | −1.675 | −      | n.a.             | −2.3 |
| 50             | 25          | 5.749                                    | 0.01  | −1.564                         | −1.261 | −1.609 | n.a.             | −3.1 |
| 50             | 27          | 5.749                                    | 0.001 | −1.567                         | −1.645 | −      | n.a.             | −3.0 |
| 40             | 40          | 0.706                                    | 0.01  | −2.997                         | −1.663 | −1.971 | n.a.             | −1.7 |
| 40             | 28          | 0.706                                    | 0.001 | <−4.1                          | −1.731 | −      | n.a.             | −2.2 |
| 40             | 40          | 2.367                                    | 0.01  | −1.926                         | −1.642 | −      | n.a.             | −2.0 |
| 40             | 28          | 2.367                                    | 0.001 | −1.750                         | −1.702 | −      | n.a.             | −2.5 |
| 40             | 40          | 4.471                                    | 0.01  | −2.181                         | −1.495 | −1.737 | n.a.             | −2.2 |
| 40             | 28          | 4.471                                    | 0.001 | −2.143                         | −1.675 | −      | n.a.             | −1.9 |
| 40             | 40          | 8.942                                    | 0.01  | −1.892                         | −1.526 | −1.847 | n.a.             | −2.7 |
| 40             | 28          | 8.942                                    | 0.001 | −1.830                         | −1.752 | −      | n.a.             | −3.7 |
| 400 °C, NNO    |             |                                          |       |                                |        |        |                  |      |
| 100            | 24          | 0.706                                    | 0.01  | −3.604                         | −3.768 | n.a.   | −1.605           | −3.0 |
| 100            | 36          | 0.706                                    | 0.001 | −3.433                         | <−4.2  | n.a.   | −1.640           | −3.2 |
| 100            | 24          | 2.367                                    | 0.01  | −2.551                         | −2.467 | n.a.   | −1.546           | −3.5 |
| 100            | 36          | 2.367                                    | 0.001 | −2.685                         | −2.230 | n.a.   | −1.607           | −2.8 |
| 100            | 24          | 4.471                                    | 0.01  | −1.831                         | −1.827 | n.a.   | −1.594           | −2.9 |
| 100            | 36          | 4.471                                    | 0.001 | −1.997                         | −1.817 | n.a.   | −1.713           | 2.8  |
| 100            | 24          | 8.942                                    | 0.01  | −1.366                         | −1.359 | n.a.   | −1.704           | −2.6 |
| 100            | 36          | 8.942                                    | 0.001 | −1.473                         | −1.306 | n.a.   | −1.812           | −2.5 |
| 25             | 24          | 0.706                                    | 0.01  | −3.566                         | −2.856 | n.a.   | −1.853           | −3.0 |
| 25             | 36          | 0.706                                    | 0.001 | <−4.1                          | −1.743 | n.a.   | −2.151           | −2.0 |
| 25             | 24          | 2.367                                    | 0.01  | −2.833                         | −2.279 | n.a.   | −1.727           | −3.0 |
| 25             | 36          | 2.367                                    | 0.001 | −2.300                         | −1.810 | n.a.   | −1.845           | −2.2 |
| 25             | 24          | 3.353                                    | 0.01  | −2.398                         | −2.104 | n.a.   | −1.685           | −3.0 |
| 25             | 36          | 3.353                                    | 0.001 | −2.097                         | −1.716 | n.a.   | −1.867           | −2.5 |
| 25             | 24          | 4.471                                    | 0.01  | −2.000                         | −1.867 | n.a.   | −1.682           | −3.0 |

(continued)

**Table 7.1** (continued)

| <i>P</i> (MPa) | Time (days) | Initial solution (mol kg <sup>-1</sup> ) |       | Final solution (log <i>m</i> ) |        |      |                  |      |
|----------------|-------------|------------------------------------------|-------|--------------------------------|--------|------|------------------|------|
|                |             | KCl                                      | HCl   | W                              | Fe     | Al   | SiO <sub>2</sub> | HCl* |
| 1              | 2           | 3                                        | 4     | 5                              | 6      | 7    | 8                | 9    |
| 25             | 36          | 4.471                                    | 0.001 | −1.696                         | −1.589 | n.a. | −1.891           | −2.6 |
| 20             | 24          | 0.706                                    | 0.01  | −3.490                         | −2.070 | n.a. | −2.392           | −1.8 |
| 20             | 36          | 0.706                                    | 0.001 | −3.577                         | −1.389 | n.a. | −2.061           | −1.2 |
| 20             | 36          | 2.367                                    | 0.01  | −2.132                         | −2.132 | n.a. | −1.886           | −3.8 |
| 20             | 36          | 2.367                                    | 0.001 | −2.131                         | −1.197 | n.a. | −2.013           | −1.7 |
| 20             | 24          | 4.471                                    | 0.01  | −1.629                         | −1.422 | n.a. | −1.827           | −1.9 |
| 20             | 24          | 4.471                                    | 0.01  | −1.645                         | −1.447 | n.a. | −1.859           | −1.7 |
| 20             | 24          | 8.942                                    | 0.01  | −1.409                         | −1.340 | n.a. | −1.820           | −2.5 |
| 20             | 36          | 8.942                                    | 0.001 | −1.234                         | −1.088 | n.a. | −1.973           | −2.6 |

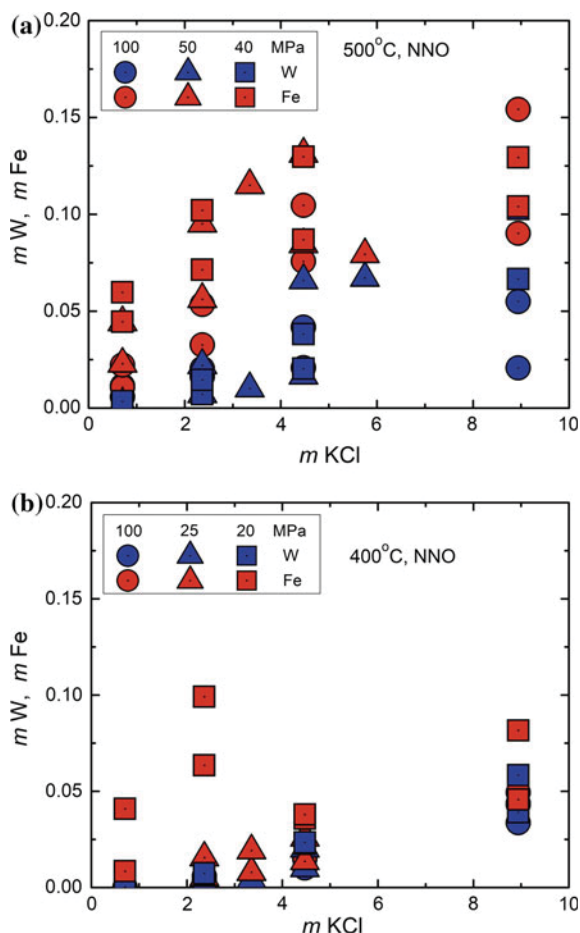
\* The molality of HCl was estimated from pH measurement of the quenched diluted solution

Among W-bearing minerals, in addition to the initial ferberite, a new phase was found represented by elongated black crystals. SEM analysis indicated the composition corresponded to a chemical composition similar to the K–W bronzes (PTB)  $K_xWO_3$ . The small quantities of PTB (<<5 wt%) found did not allow for positive identification using X-ray diffraction. The largest crystals (10–50 μm thick) were chosen for microprobe analysis. The analytical results indicate their composition at 500 °C, 100 MPa corresponded to the formula  $K_{0.24\pm0.01}WO_3$  (19 tests, runs in 25 and 40 wt% KCl and 0.1 mHCl), at 50 MPa  $K_{0.23\pm0.01}WO_3$  (11 tests, run in 25 wt% KCl and 0.1 mHCl), and at 40 MPa  $K_{0.21\pm0.02}WO_3$  (15 tests, run in 40 wt% KCl and 0.1 mHCl). We did not find additional system components present in PTB. A detailed study of ferberite crystals showed however, that in some crystals there occurred an increase in the W/Fe molar ratio during the experiment and an accompanying accumulation of potassium was observed. One can assume that such crystals represented thin growths of ferberite and PTB.

## 7.5 Thermodynamic Simulations

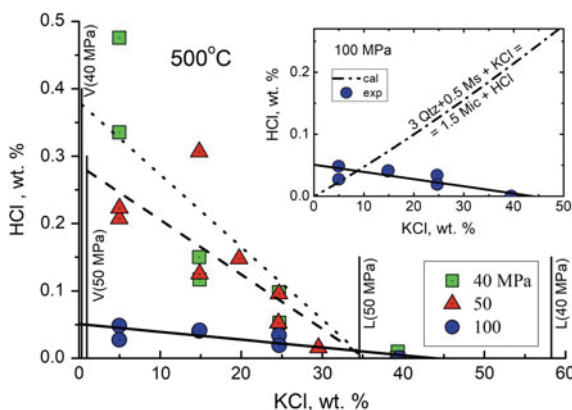
In solving the problem of the behavior and conditions of ore deposition in hydrothermal deposits, an important role is played by the solubility of ore minerals and the forms of the existence of ore components in their equilibrium solutions. The main component of hydrothermal fluid in tungsten deposits in greisenes is alkali metal chlorides, which concentrations vary widely from 0 to 60 wt% (Wood and Vlassopoulos 1989; Wood and Samson 2000; Gao et al. 2014). In these solutions, according to various researchers, tungsten could exist in the form of tungsten acid  $H_2WO_4^0$ , the

**Fig. 7.4** W and Fe concentrations ( $\text{mol kg}^{-1}$ ) in equilibrium with ferberite in the KCl–HCl–H<sub>2</sub>O system buffering by QMM and NNO at 500 (a) and 400 °C (b)



products of its dissociation  $\text{HWO}_4^-$ ,  $\text{WO}_4^{2-}$  (Ivanova and Khodakovskii 1972) and polymerization  $\text{W}_4\text{O}_{13}^{2-}$  (Bryzgalin 1976),  $\text{H}_7(\text{WO}_4)_6^{5-}$ ,  $\text{H}_{10}(\text{WO}_4)_6^{2-}$  (Wesolowski et al. 1984), associations with alkaline metal ions  $\text{NaHWO}_4^0$  (Wood and Vlassopoulos 1989; Wood and Samson 2000), chlorine  $\text{WO}_2\text{Cl}_2^0$  (Veispāls 1979) and mixed form such as  $\text{HWO}_3\text{Cl}^0$ ,  $\text{NaWO}_3\text{Cl}^0$  (Khodorevskaya et al. 1990; Kolonin and Shironosova 1991). It is generally not possible to identify species, as the existing experimental data are not sufficient for this purpose. Therefore, the relevance of studies of W complexation in hydrothermal systems in connection with the problem of transport and deposition of tungsten minerals (Eugster 1986; Kolonin and Shironosova 1991; Volina and Barabanov 1995) is still unaddressed.

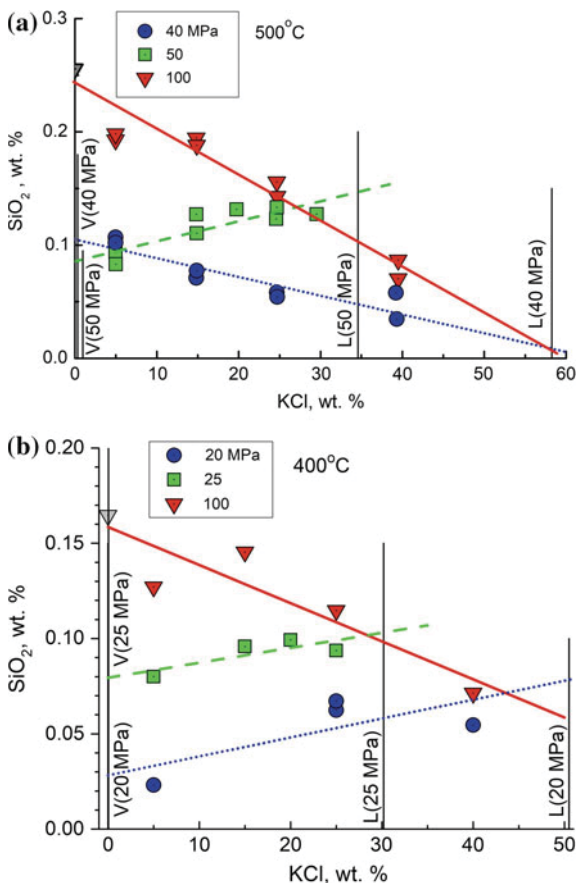
To describe the solubility of W-containing minerals at high  $T$ - $P$  parameters, there are mutually agreed thermodynamic data (equilibrium constants and Gibbs free energies) for only 5 species W(VI):  $\text{H}_2\text{WO}_4^0$ ,  $\text{HWO}_4^-$ ,  $\text{WO}_4^{2-}$ ,  $\text{NaHWO}_4^0$  and  $\text{NaWO}_4^-$  (Wood and Samson 2000). For the species  $\text{KHWO}_4^0$  and  $\text{KWO}_4^-$  approximation of



**Fig. 7.5** Total quench HCl results as a function of KCl concentration in the experiments on ferberite solubility in Qtz-Mic-Ms-Ni-NiO buffered system at 500 °C and 40, 50, 100 MPa and their correlation with calculated values of HCl and KCl of the alumina-silicate buffer assemblage at 100 MPa. The dotted, dashed and solid lines are results of linear fit in addition to the L, V lines

the association constants has been evaluated. The data on particles and complexes of W(V) are completely absent, although in experiments on the solubility of  $\text{WO}_3$  and  $(\text{Fe}, \text{Mn})\text{WO}_4$  in NaCl solutions, the formation of tungsten blue with a variable content of W(VI)/W(V) occurred (Bryzgalin 1976; Wesolowski et al. 1984; Manning and Henderson 1984; Wood and Vlassopoulos 1989; Zaraisky 1995; Redkin et al. 1999). These compounds, according to the composition and X-ray data, corresponded to sodium tungsten bronzes,  $\text{Na}_x\text{WO}_3$ , where  $x = 0.1\text{--}0.4$ , and were formed already at  $f\text{O}_2$  with the oxygen buffer corresponding to  $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$  (Red'kin 2000). The effect of  $f\text{O}_2$  on the solubility of wolframite and its extreme members of ferberite and hubnerite (huebnerite) ( $\text{MnWO}_4$ ) has not been considered.

We used numerical simulation of the Qtz + Mic + Ms + Ferb with KCl–HCl– $\text{H}_2\text{O}$  solution at 400–500 °C and 100 MPa in an open system with  $f\text{O}_2$  corresponding to the Ni–NiO (NNO:  $f\text{O}_2 = 10^{-22.423}$  Pa at 400 °C– $10^{-17.706}$  Pa at 500 °C) and  $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$  (HM:  $10^{-13.63}$  Pa at 500 °C) buffers to determine the composition of the W complexes (Robie and Hemingway 1995). Determination and refinement of thermodynamic properties of aqueous solution species is solved using the software package HCh (Shvarov and Bastrakov 1999) and the program supporting technology OLE Automation (Shvarov 2008), realized in the program OptimA (Shvarov 2015). Thermodynamic properties of most simple particles and complexes  $\text{K}^+$ ,  $\text{KCl}^0$ ,  $\text{KOH}^0$ ,  $\text{Na}^+$ ,  $\text{NaCl}^0$ ,  $\text{NaOH}^0$ ,  $\text{SiO}_2\text{aq}^0$ ,  $\text{HSiO}_3^-$ ,  $\text{Fe}^{2+}$ ,  $\text{WO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{H}^+$ , were taken from SUPCRT'92 (Johnson et al. 1992; Shock et al. 1997), aluminum species  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{HAIO}_2^0$ ,  $\text{Al}(\text{OH})_0$ ,  $\text{AlO}_2^-$ ,  $\text{Al}(\text{OH})_4^-$  by Pokrovskii and Helgeson (1995), Gibbs Free energy of  $\text{HCl}^0$ , by Hemley et al. (1992),  $\text{FeCl}^+$ ,  $\text{FeCl}_2^0$  by Wood and Samson (2000). Free energy and HKF parameters of hydroxo and chloride complexes  $\text{Fe(II): Fe}(\text{OH})^-$ ,  $\text{FeOaq}^0$ ,  $\text{HFeO}_2^-$ ,  $\text{FeCl}^+$  and  $\text{FeCl}_2^0$  are calculated from the equilibrium constants of the hydrolysis reactions presented in Wood and Samson



**Fig. 7.6** The dependence of dissolved silica (in wt%) from Qtz-Mic-Ms buffers on the initial KCl concentration in experiments at 500 (a) and 400 °C (b), their approximation by linear fit (solid and dashed lines) and calculated quartz solubility in relation to Si species composition at 1000 bar. Vertical lines show KCl concentration in vapor 'V' and liquid 'L' phases at the corresponding pressure in MPa

(2000). For  $\text{Fe(III)}$ :  $\text{FeOH}^{2+}$ ,  $\text{Fe(OH)}_2^+$ ,  $\text{Fe(OH)}_3^0$ ,  $\text{Fe(OH)}_4^+$  hydroxocomplexes the best convergence of the calculated and data free energies was obtained using the approximation of the stability constants of the complexes (Wood and Samson 2000) modified Ryzhenko-Bryzgalin equation (Ryzhenko 1981; Bryzgalin and Ryzhenko 1981; Bryzgalin and Rafalsky 1982). The contribution of  $\text{Fe(III)}$  species to the total iron concentration was negligible (Wood and Samson 2000).

We did not consider the species of the  $\text{KFeCl}_3^0$  composition, although according to Tagirov (1998), the contribution of these particles to the total solubility of the iron-containing phases in highly concentrated water-salt solutions may be dominant.

The activity coefficients of aqueous species with were calculated using an extended Debye-Hückel equation

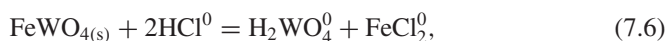
$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + Ba\sqrt{I}}, \quad (7.5)$$

where  $I$  ( $\text{mol kg}^{-1}$ ) stands for ionic strength of the solution,  $A$  and  $B$  represent the Debye Hückel coefficients for pure solvent dependent on  $P$ ,  $T$ ;  $z_i$  is the charge and  $a$  is the ion size parameter that was accepted after Rafalsky (1973) to be equal 4.5 Å for all species.

The free energies of formation of quartz (Qtz) and microcline (Mic) are taken as the basis for solid mineral phases (Robie et al. 1978). The free energies of Ab (albite), And (andalusite), Ms, Prg (paragonite), Pf (pyrophyllite) were corrected according to experimental constants of hydrolysis reactions (Hemley and Jones 1964) and taken as stable phases in the system  $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{HCl}$  at 500–400 °C and 100 MPa.

For reaction (7.1), which served in our experiments as an acid-base buffer, the accepted value for the equilibrium ratio  $\log m\text{KCl}/m\text{HCl} = 2.08$  (at 500 °C, 100 MPa) and 2.70 (at 400 °C, 100 MPa) (Hemley 1959; Redkin 1983). This also led to an aluminum saturation concentration corresponding to our experimental data (approximately  $10^{-4}$ – $10^{-5}$   $\text{mol kg}^{-1}$   $\text{H}_2\text{O}$ ).

When calculating the free energies of ferberite, we used the equilibrium constants of the reaction of dissolving ferberite calculated at 400 and 500 °C and 100 MPa according to Wood and Samson (2000):



$\text{pK}(6) = 3.2$  and  $3.0$ , respectively.

When determining the composition of aqueous species and the valence state of tungsten in solutions (see Table 7.1) with the parameters of the experiments, the following assumptions were taken into account;

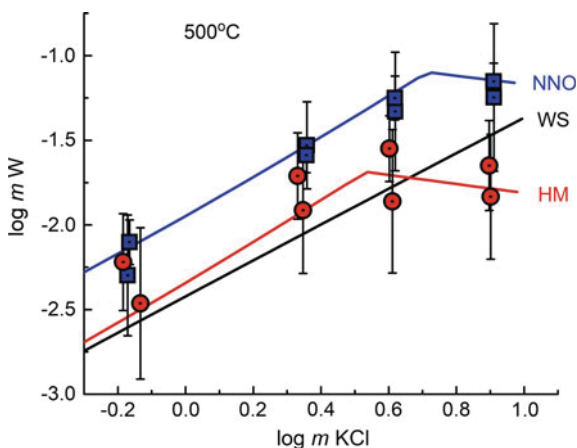
1. Most aqueous tungsten was assumed to be present as complex of W(V) as the cooled solutions were W, colorless and transparent despite high concentrations ( $m\text{W}_{\text{total}} > 0.002$   $\text{mol kg}^{-1}$ ). When performing chemical analyzes on tungsten, using the colorimetric method with bromopyrogallol red in the presence of cetylpyridinium bromide as a surfactant (Mamedova et al. 2004), it was noted that the solutions after the experiments when mixed with a strong alkali, with the addition of hydroxylamine, actively interacted, producing small ammonia bubbles (alkaline reaction of the wet indicator paper in the atmosphere of bubbles). These gas bubbles dissolved in the liquid phase. It is known (Brikun et al. 1967) that strong reducing agents ( $\text{HI}$ ,  $\text{H}_2\text{S}$ ,  $\text{SnCl}_2$ , zinc dust, etc.) reduce hydroxylamine to  $\text{NH}_3$ . Since there were no other reducing agents in the solutions, it is reasonable to assume that the species W(V) or even W(IV) behaved as the reducing agent in the analyzed solutions.

An additional but indirect argument for the presence of W(V) can be potassium tungsten bronzes  $K_xWO_3$  (PTB), where  $x = 0.20\text{--}0.24$ , which is formed in the experiments and represents compounds of W(V, VI).

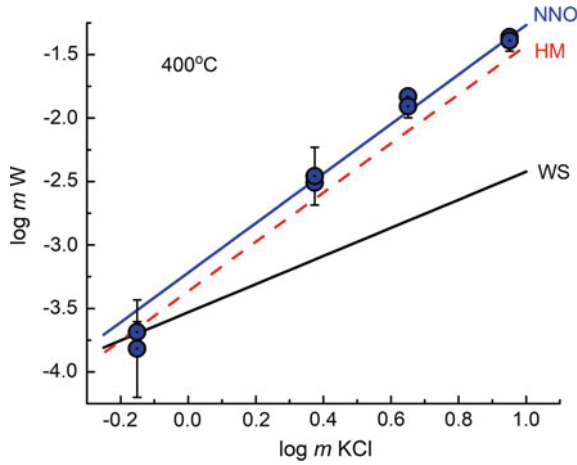
- W(V) in solution at high temperature is represented by monomeric and polymeric species, which may include  $K^+$ ,  $Cl^-$ ,  $OH^-$ ,  $H_2O$ . Silica-12-tungsten acid and its salts  $K_{4-x}H_x[SiW_{12}O_{40}] \cdot nH_2O$  ( $x = 0\text{--}4$ ,  $n = 5, 14, 24$  or  $30$ ), as well as other silica heteropolytungstate compounds were not formed in appreciable amounts. This follows from the analysis of solubility data of quartz (Table 7.1 and Fig. 7.6a, b) at 500 and 400 °C and 100 MPa.
- Changes in the acidity of the solutions may be mainly due to hydrolysis or dissociation of tungsten compounds upon cooling, since ferrous chloride species,  $FeCl^+$  and  $FeCl_2^0$ , which are stable in the test mode, do not hydrolyze when cooled to room temperature, but completely dissociate into  $Fe^{2+}$  and  $Cl^-$  without changing  $mHCl_{total}$  ( $mHCl^0 + mH^+$ ).

For test the calculated and experimental data of congruent and incongruent (with the formation of PTB-02,  $K_{0.2}WO_3$ ) solubility of ferberite, presented in Table 7.1, we examined more than 15 W(V) species containing from 1 to 6 tungsten atoms and having a charge of +1 to −3, as well as 5 anionic species with a charge of −1 to −3, containing both W(V) and 20–66 mol% W(VI). The  $KHWO_4^0$  and  $KWO_4^-$  species proposed in Wood and Samson (2000), line WS in Figs. 7.7 and 7.8 were the dominant contributors to the solubility of ferberite in strong KCl solutions, but did not reflect the effect of  $fO_2$ , were omitted from consideration.

We assumed that W(V) compounds as well as compounds W(VI) compounds in a hydrothermal solution will have similar structure. This was taken into consideration when selecting the composition of possible aqueous species W(V).



**Fig. 7.7** Influence of  $mKCl$  on  $mW$  in a solution equilibrated with ferberite in the QMM buffered system at 500 °C and 100 MPa by experimental (symbols) and calculated (lines) data. The WS line is from calculations by Wood and Samson (2000)



**Fig. 7.8** Influence of  $m\text{KCl}$  on  $m\text{W}$  in a solution equilibrated with ferberite in the QMM buffered system at 400 °C and 100 MPa by experimental (symbols) and calculated (lines) data. The WS line is from calculations by Wood and Samson (2000)

According to the data presented in Table 7.1, the total concentrations of iron and tungsten in the solutions after the experiment were differed. This could be due to the initial purity of synthetic ferberite (a slight excess of iron oxide), an insufficient amount of quartz, and the formation of a containing phase in the course of the experiment, i.e. potassium tungsten bronzes (PTB). The congruent solubility of ferberite in potassium chloride solution, with an acidity given by Qtz-Mic-Ms buffer, can be calculated by the equation

$$m\text{FeWO}_4 = \sqrt[\alpha+1]{(m\text{W}_{\text{total}})^\alpha \times m\text{Fe}_{\text{total}}}, \quad (7.7)$$

where  $\alpha = \sum_i \frac{\alpha_i}{i}$ ,  $\alpha_i = \frac{i \cdot m\text{W}_i}{m\text{W}_{\text{total}}}$  mol fractions of fluid species containing the same number  $i$  of atoms  $\text{W}$ , taking into account the fractions of species of different degrees of polymerization in calculations using the obtained equilibrium constants. Considering that the main contribution to  $\text{W}_{\text{total}}$  is made by  $\text{W(V, VI)}$  species in the form of monomers, Eq. (7.7) can be simplified to the form

$$m\text{FeWO}_4 = \sqrt{(m\text{W}_{\text{total}} \times m\text{Fe}_{\text{total}})}, \quad (7.8)$$

representing the geometric mean of the concentrations of tungsten and iron. In Fig. 7.7, square and round symbols show the solubility of ferberite calculated using Eq. (7.8) for NNO and HM buffers, respectively. Extreme concentrations of  $\text{W}_{\text{total}}$  and  $\text{Fe}_{\text{total}}$  are accepted for the magnitude of the  $m\text{FeWO}_4$  definition error.

The best agreement of experimental and calculated data (see Fig. 7.7) at 500 °C and 100 MPa was achieved for two newly introduced species  $\text{WO}_3^-$  (or  $\text{H}_2\text{W}^{\text{V}}\text{O}_4^-$ )

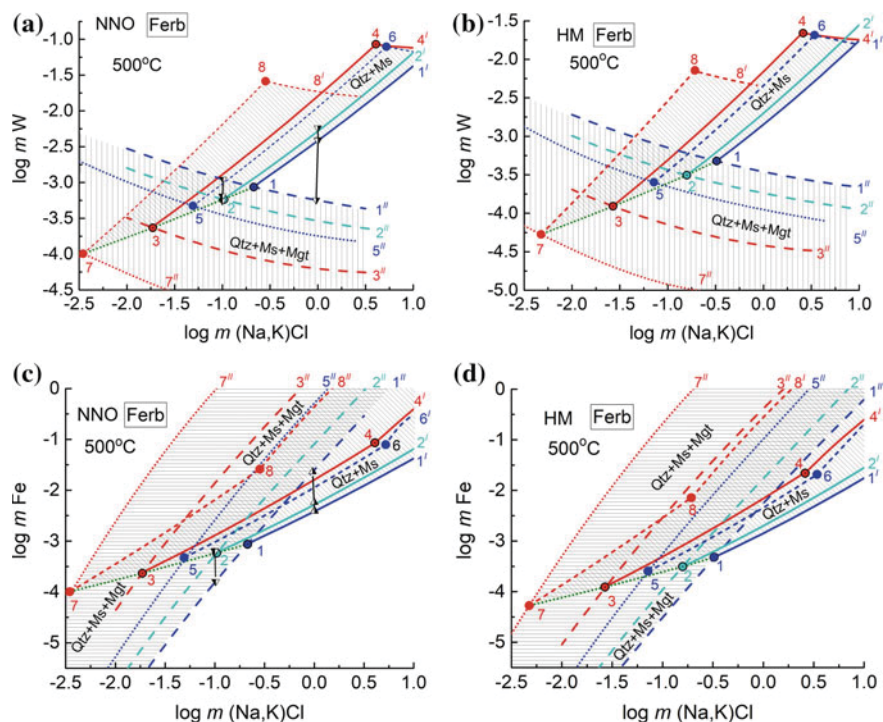
and  $\text{H}_2\text{W}_2\text{O}_7^-$  ( $\text{H}_2\text{W}^{\text{V}}\text{W}^{\text{VI}}\text{O}_4^-$ ). According to calculations,  $\text{FeCl}_2^0$  are the predominant iron species in solution at both NNO and HM oxygen buffers over the entire KCl concentration range studied. The structure of the predominant tungsten species, conversely, depended on both  $f\text{O}_2$ , and  $m\text{KCl}$ . At HM buffer conditions the W(VI) content ranged from 32 to 43.5% of  $m\text{W}_{\text{total}}$  in the  $m\text{KCl}$  range from 0.3 to 7.7. At low concentrations of KCl, tungsten-bearing species  $\text{WO}_3^-$ ,  $\text{HWO}_4^-$ ,  $\text{H}_2\text{W}_2\text{O}_7^-$  (in order of importance) prevailed, while in concentrated solutions the  $\text{H}_2\text{W}_2\text{O}_7^-$  species dominated.

At NNO buffer conditions, calculations indicate the  $\text{WO}_3^-$  and  $\text{H}_2\text{W}_2\text{O}_7^-$  species dominated in the  $m\text{KCl}$  range investigated. W(VI) concentrations increased in solution from 9 to 34.8% with increasing  $m\text{KCl}$  from 0.3 to 5.3. Incongruent dissolution of Ferb with concurrent formation of PTB and a slight decrease in both  $m\text{W}_{\text{total}}$  and fraction of W(VI) in solution (Fig. 7.7) shows good agreement between calculated and experimental data.

The influence of potassium chloride concentration on solubility of the ferberite in the solutions at 400 °C, 100 MPa, NNO buffer and at the acidity given by Mic-Ms-Qtz buffer is shown in Fig. 7.8. The slope of  $m\text{W}$  with  $m\text{K}$  at 400 °C is steeper than at 500 °C. This indicates that there are aqueous tungsten species present that contain more than 2 W atoms. The best agreement between the experimental and calculated data (see Fig. 7.8) was obtained by introducing the species  $\text{W}_5\text{O}_{16}^{3-}$  (or  $\text{W}^{\text{V}}\text{W}_4^{\text{VI}}\text{O}_{16}^{3-}$ ) previously proposed in the work (Redkin and Kostromin 2010). According to calculations, the fraction of the  $\text{W}_5\text{O}_{16}^{3-}$  species increases dramatically at  $m\text{KCl} > 0.05$  reaching 99% in the solution containing 0.7  $m\text{KCl}$ . At the same time, the share of W(V) is 20% of the particles concentration of  $\text{W}_5\text{O}_{16}^{3-}$ . In Fig. 7.8 (WS line) also shows the results of calculations based on data (Wood and Samson 2000) using  $\text{KHWO}_4^0$  and  $\text{KWO}_4^-$  species.

Concentrations of sodium salts in natural hydrothermal solutions are typically greater than that of potassium, therefore we made calculations for ferberite solubility in solutions of NaCl–KCl–HCl. Since the composition of ore-bearing solutions can only be assumed, but since it is known the hydrothermal solutions produce quartz-muscovite alteration in the host rocks, it is possible to speculate on geochemical boundary conditions. The Qtz + Ms association field at 500 and 400 °C, 100 MPa and constant  $m\text{Cl}$  is limited by the following non-variant points: Qtz–Ab–Mic–Ms (1), Qtz–Ab–Prg–Ms (2) and Qtz–And–Prg–Ms (3 at 500 °C) or Qtz–Pf–Prg–Ms (3 at 400 °C) after Hemley and Jones (1964). If the concentration of chlorides in a system changes, then non-variant points turn into the hydrolysis equilibria, which determine the  $m\text{KCl}/m\text{HCl}$  and  $m\text{NaCl}/m\text{HCl}$  ratios. Thus, the solubility of ferberite on the lines of hydrolysis reactions of aluminosilicates will correspond to extreme values. The systems in which iron oxides are present are also of interest. Calculations show that at low chloride concentrations, magnetite accompanies ferberite.

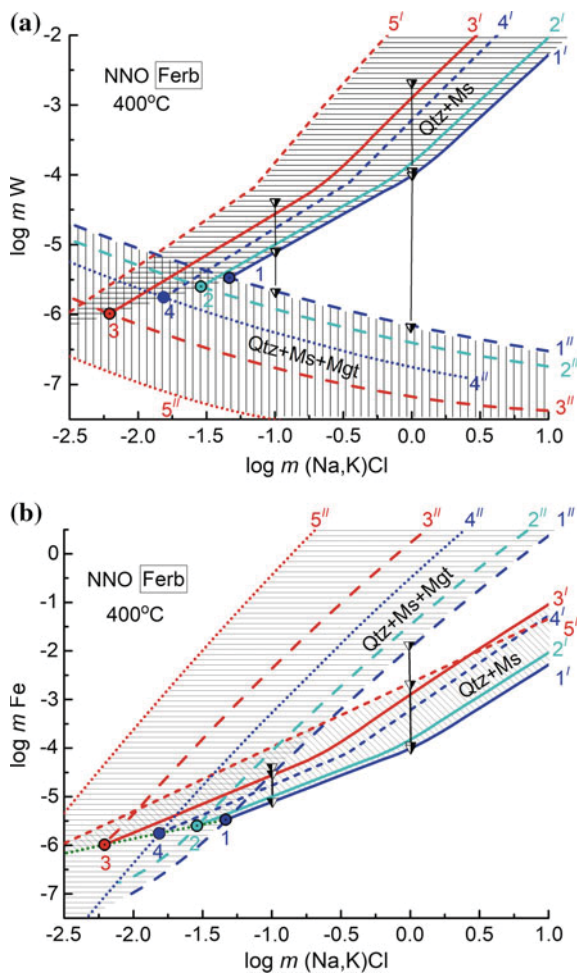
Figures 7.9 and 7.10 show the results of the calculations at 400 and 500 °C and pressure of 100 MPa. As expected, the solubility of Ferb increases with the increasing temperature,  $m\text{Cl}$  ( $m\text{NaCl} + m\text{KCl}$ ),  $f(\text{H}_2)$ ,  $m\text{KCl}/m\text{HCl}$  (or when changing associations 1 → 3) and decreases in the presence of Mgt. The maximum solubility of ferberite is found in KCl solutions equilibrated with Qtz–And–Ms at 500 °C or



**Fig. 7.9** The projections of 3D surfaces of ferberite solubility on the  $m(\text{Na}, \text{K})\text{Cl}$ – $m\text{W}$  and  $m(\text{Na}, \text{K})\text{Cl}$ – $m\text{Fe}$  plane at 500 °C, 100 MPa, NNO (a, c) and HM (b, d) buffers in chloride solutions controlled by various alumina-silicate assemblages. Legend 1—nonvariant point (NP) Qtz + Ab + Mic + Ms + Ferb + Mgt; 2—Qtz + Ab + Prg + Ms + Ferb + Mgt; 3—Qtz + And + Ms + Prg + Ferb + Mgt; 4—Qtz + And + Ms + Prg + Ferb + PTB-02; 5—Qtz + Mic + Ms + Ferb + Mgt (NaCl free solutions); 6—Qtz + Mic + Ms + Ferb + PTB-02 (no NaCl); 7—Qtz + And + Ms + Ferb + Mgt (no NaCl); 8—Qtz + And + Ms + Ferb + PTB-02 (no NaCl); 1', 2', 4, 6—lines of saturation of solutions with Ferb (congruent dissolution); 4' and 6'—Ferb + PTB, 1'', 2'', 3'', 4'', 5'', 7'', 8''—Ferb + Mgt, correspondingly; the shaded areas show the limits of variation in the concentrations of tungsten (a, c) and iron (b, d) for the Qtz + Ms + Ferb and Qtz + Ms + Ferb + Mgt, respectively

Qtz-Pf-Ms at 400 °C. Further change in the composition of solution towards reduction of  $m\text{KCl}/m\text{HCl}$  will cause the formation of andalusite (or pyrophyllite), and in solutions containing fluorine—topaz. Therefore, solutions saturated with ferberite, marked by hatching in these figures, are of practical interest for modeling tungsten ore formation. From the data obtained, it follows that at 500 °C the change in  $f(\text{O}_2)$  from NNO to HM buffer reduces the tungsten concentrations in solution by 1.5–2.7 times, and at 400 °C by 1.4 times.

The influence of aluminosilicate assemblage and the presence of magnetite on the content of tungsten and iron in solution saturated with ferrite is of interest. Figure 7.9a, c and 7.10a, b triangular symbols show trends of the changing  $m\text{W}$  and  $m\text{Fe}$  in solution initially equilibrated with the Qtz-Ms-Ferb assemblage, then interacting with wall



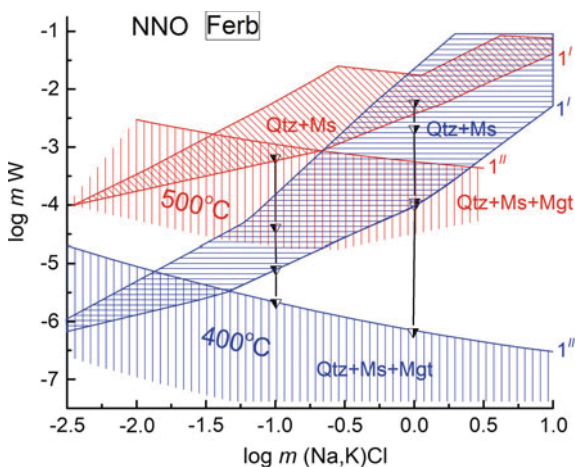
**Fig. 7.10** The projections of 3D surfaces of ferberite solubility on the  $m(\text{Na}, \text{K})\text{Cl}$ – $mW$  (a) and  $m(\text{Na}, \text{K})\text{Cl}$ – $m\text{Fe}$  (b) plane at  $400^{\circ}\text{C}$ , 100 MPa, NNO buffer in chloride solutions controlled by various alumina-silicate assemblages. *Legend* 1—nonvariant point  $\text{Qtz} + \text{Ab} + \text{Mic} + \text{Ms} + \text{Ferb} + \text{Mgt}$ ; 2—ND  $\text{Qtz} + \text{Ab} + \text{Prg} + \text{Ms} + \text{Ferb} + \text{Mgt}$ ; 3— $\text{Qtz} + \text{Pf} + \text{Ms} + \text{Prg} + \text{Ferb} + \text{Mgt}$ ; 4— $\text{Qtz} + \text{Mic} + \text{Ms} + \text{Ferb} + \text{Mgt}$  (no NaCl added); 5— $\text{Qtz} + \text{Pf} + \text{Ms} + \text{Ferb} + \text{Mgt}$  (no NaCl); 6— $\text{Qtz} + \text{Mic} + \text{Ms} + \text{Ferb} + \text{PTB-02}$  (no NaCl); 1', 2', 3', 4', 5'—congruent dissolution of Ferb; 1'', 2'', 3'', 4'', 5''—Ferb + Mgt; the shaded areas show the limits of variation in the concentrations of tungsten (a) and iron (b) for the  $\text{Qtz} + \text{Ms} + \text{Ferb}$  and  $\text{Qtz} + \text{Ms} + \text{Ferb} + \text{Mgt}$ , respectively

rocks containing Mic, Ab, Mgt. In solutions containing  $0.76 m\text{NaCl} + 0.24 m\text{KCl} + 0.01 m\text{HCl}$ , equilibrated at  $500^{\circ}\text{C}$  with  $\text{Qtz}$ – $\text{Ms}$ – $\text{Ferb}$  assemblage, the smallest change (1.4 times) is due to the appearance of Mic and Ab, while saturation of the solution with magnetite reduces the initial  $mW$  by 10 times. In  $0.1 m\text{Cl}$  solution of  $0.076 m\text{NaCl} + 0.024 m\text{KCl} + 0.001 m\text{HCl}$ , the  $mW$  variations are less obvious

and have the opposite tendency, i.e. the appearance of magnetite in association with Qtz-Ms-Ferb leads to a slight decrease in  $mW$ , while saturation of the solution with albite, microcline and magnetite from side rocks increases the solubility of ferberite ( $mW$ ) (see Fig. 7.9a).

The solution containing  $0.76 \text{ mNaCl} + 0.24 \text{ mKCl} + 0.01 \text{ mHCl}$ , equilibrated at  $400^\circ\text{C}$  and  $100 \text{ MPa}$  with Qtz-Ms-Ferb assemblage, contains  $0.002 \text{ mW}$ . The interaction of such a solution with side rocks containing Mic or Mic + Ab, leads to the deposition of 94.5–95.2% tungsten in the form of ferberite from the solution, while the presence of Mgt in wall rocks reduces the concentration of tungsten in the affecting solution by 99.97% (Fig. 7.10). Tungsten content in the  $0.076 \text{ mNaCl} + 0.024 \text{ mKCl} + 0.001 \text{ mHCl}$  equilibrium solution with the Qtz-Pf-Ms-Ferb assemblage is 50 times lower, than in the  $1.0 \text{ mCl}$  solution. Although tungsten deposition from this solution due to geochemical barriers associated with the appearance of Mic and Mgt in the host or wall rocks is very significant (from 80 to 95%), solutions containing  $0.1 \text{ mCl}$  cannot be considered promising for the formation large deposits of tungsten ores associated with granites.

Particular attention should be paid to the effect of temperature and wall rock mineralogy on the solubility of ferberite. Figure 7.11 shows a case when the chloride solutions containing  $1.0$  and  $0.1 \text{ mCl}$  are first equilibrated at  $500^\circ\text{C}$  and  $100 \text{ MPa}$  with Qtz-Ms-Ferb assemblage and then isobarically cooled to  $400^\circ\text{C}$ , imposing the solutions to interact with wall rocks containing feldspars and magnetite. Calculations indicate that the decrease in temperature of hydrothermal ore-bearing solution and its interaction with both feldspars and magnetite leads to the deposition of 99% of



**Fig. 7.11** Influence of temperature,  $m\text{KCl}$  and wall rock minerals (Mic, Ab, Mgt) on  $mW$  change in solutions initially equilibrated with the quartz-muscovite-ferberite assemblage at  $500^\circ\text{C}$ ,  $100 \text{ MPa}$ , NNO (the projections of 3D surfaces of ferberite solubility on the  $m(\text{Na}, \text{K})\text{Cl}-mW$  plane). Legend 1'—nonvariant equilibria Qtz + Ab + Mic + Ms + Ferb; 1''—Qtz + Ab + Mic + Ms + Ferb + Mgt

tungsten. Moreover, taking into account the high solubility of ferberite at 500 °C and 100 MPa in 0.1 *m*Cl solution ( $6.5 \times 10^{-4}$  *m*W), such solutions can be considered as ore-bearing ones.

The presented results of thermodynamic modeling were performed for a homogeneous region of NaCl–KCl–HCl–H<sub>2</sub>O fluid. In the region of immiscibility, the water-salt fluid splits into two equilibrium fluids of different densities, containing different amounts of HCl and (Na, K)Cl, which have a major influence on the peculiarity of dissolving ferberite in coexisting fluid phases.

The thermodynamic calculations used for a homogeneous solution cannot be used for the region of the fluid immiscibility (Redkin et al. 2015). As soon as apparent solubility of ferberite on concentration of KCl in two-phase region corresponds to Eq. (7.4) we can calculate the solubility of ferberite in the V- and L-phases of KCl fluid. The results of calculations in wt% are shown in Table 7.2. The correlations between apparent solubility of ferberite and concentration of KCl in the two-phase region are given in the right-hand column. The values of  $S_{\text{FeWO}_4}$  obtained clearly demonstrate its dependence on  $f\text{O}_2$ . Otherwise the ferberite dissolution has to be considered as a redox reaction in range  $f\text{O}_2$  from  $10^{-17.7}$  (NNO) to  $10^{-13.63}$  Pa (HM) at 500 °C. Taking in account that the predominant valence of iron relates to Fe(II) as in ferberite as well as in solute species, because high dissolution of iron in the system studied, W can change valance only from W(VI) in ferberite to W(V or IV) in solution.

**Table 7.2** Estimated values of ferberite solubility in vapor and liquid phases of the fluid KCl–HCl–H<sub>2</sub>O

| <i>T</i> (°C) | <i>P</i> (MPa) | V-phase (wt%) |                   | L-phase (wt%) |                   | <i>f</i> O <sub>2</sub> | Correlations used                                              |
|---------------|----------------|---------------|-------------------|---------------|-------------------|-------------------------|----------------------------------------------------------------|
|               |                | KCl           | FeWO <sub>4</sub> | KCl           | FeWO <sub>4</sub> | Buffer                  | Ferberite solubility ( <i>S</i> ) (wt%)                        |
| 500           | 50             | 0.96          | 0.21              | 34.59         | 2.03              | NNO                     | $S = 0.154 + 0.0543 \cdot C_{\text{KCl}} (\pm 0.15)$           |
| 500           | 40             | 0.32          | 0.50              | 58.25         | 2.57              | NNO                     | $S = 0.493 + 0.0356 \cdot C_{\text{KCl}} (\pm 0.11)$           |
| 500           | 50             | 0.96          | 0.19              | 34.59         | 0.77              | HM                      | $S = 0.178 + 0.017 \cdot C_{\text{KCl}} (\pm 0.15)$            |
| 500           | 40             | 0.32          | 0.34              | 58.25         | 0.36              | HM                      | $S = 0.342 + 0.00032 \cdot C_{\text{KCl}} (\pm 0.15)$          |
| 400           | 25             | 0.067         | 0.001             | 30.00         | 0.41              | NNO                     | $S = 5 \cdot 10^{-5} + 0.0136 \cdot C_{\text{KCl}} (\pm 0.15)$ |
| 400           | 20             | 0.011         | 0.1               | 51.16         | 1.33              | NNO                     | $S = 0.101 + 0.024 \cdot C_{\text{KCl}} (\pm 0.15)$            |

## 7.6 Conclusions

1. Ferberite dissolution in KCl solutions under pH and  $f\text{O}_2$  buffered conditions (Qtz-Mic-Ms, and NNO or HM) at 400–500 °C behaves both congruently as well as incongruently with accompanying potassium tungsten bronzes formation (PTB),  $\text{K}_x\text{WO}_3$ , ( $x = 0.2\text{--}0.3$ ).
2. Using bulk composition data, the congruent and apparent solubility of ferberite at 400 and 500 °C in homogeneous KCl–HCl solutions at  $P = 100$  MPa and in the region of fluids immiscibility at  $P = 20, 25, 40$ , and 50 MPa has been estimated. Tungsten concentration values do not show strong pressure dependence, however, there is some solubility increase accompanying pressure decreases in  $m\text{KCl} < 3 \text{ mol kg}^{-1}$  solutions.
3. The data at  $P = 100$  MPa and  $m\text{KCl}$  from 0.7 to 3  $\text{mol kg}^{-1}$  suggest the general contribution of total tungsten solubility may favor the mononuclear species which, in turn, causes increased acidity of the quenched solution in the homogeneous region. Conversely, in 4.0–8.9  $m\text{KCl}$  solutions and in the region of fluids immiscibility at 500 °C, pressure of 40, 50 MPa and  $f\text{O}_2 = 10^{-17.7}$  Pa (NNO), we identified polynuclear tungsten(V, VI) species contributing to increased alkalinity during quench.
4. As has been shown in thermodynamic calculations at  $P = 100$  MPa, the predominant aqueous species of tungsten in KCl–HCl solutions at  $f\text{O}_2 = f\text{O}_2(\text{NNO})$  may be W(V, VI) species:  $\text{WO}_3^-$ ,  $\text{HWO}_4^-$ ,  $\text{H}_2\text{W}_2\text{O}_7^-$  at 500 °C and  $\text{HWO}_4^-$ ,  $\text{W}_5\text{O}_{16}^{3-}$  at 400 °C.
5. The total  $m\text{W}$  in equilibrium with ferberite in the aluminosilicate buffered systems depends upon  $m\text{Cl}$ ,  $T$  and  $f\text{O}_2$ . Deposition of tungsten from ore-bearing solutions is due to interaction with wall rocks containing feldspars, and iron oxides and decrease of temperature. In the magnetite bearing system, the equilibrium tungsten concentration does not exceed  $2 \cdot 10^{-5} \text{ mol kg}^{-1}$  at 400 °C. Therefore, aqueous tungsten mobility should decrease sharply in iron-enriched rocks.

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