

Article

Phlogopite-Forming Reactions as Indicators of Metasomatism in the Lithospheric Mantle

Oleg Safonov ^{1,2,3,*}, Valentina Butvina ¹ and Evgenii Limanov ¹

¹ D.S. Korzhinskii Institute of Experimental Mineralogy, Russian Academy of Sciences, Academician Ossipyan str., 4, Chernogolovka, Moscow region 142432, Russia; valkil@yandex.ru (V.B.); limanov.z@gmail.com (E.L.)

² Geological Department, Lomonosov Moscow State University, Vorob'evy Gory, Moscow 119899, Russia

³ Department of Geology, University of Johannesburg, Auckland Park, Johannesburg 2006, South Africa

* Correspondence: oleg@iem.ac.ru; Tel.: +7-910-472-8084

Received: 4 October 2019; Accepted: 2 November 2019; Published: 6 November 2019



Abstract: Phlogopite is widely accepted as a major mineral indicator of the modal metasomatism in the upper mantle within a very wide P–T range. The paper reviews data on various phlogopite-forming reactions in upper-mantle peridotites. The review includes both descriptions of naturally occurring reactions and results of experiments that model some of these reactions. Relations of phlogopite with other potassic phases, such as K-richterite, sanidine and K-titanates, are discussed. These data are taken as a basis for thermodynamic modeling of the phlogopite-forming reactions for specific mantle rocks in terms of $\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{K}_2\text{O}})$ diagrams (pseudosections) using the Gibbs free energy minimization. These diagrams allow estimation of potassium–water activity relations during metasomatic transformations of mantle rocks, prediction sequences of mineral assemblages with respect to these parameters and comparison of metasomatic processes in the rocks of different composition. This approach is illustrated by examples from peridotite xenoliths from kimberlites.

Keywords: upper mantle; phlogopite; mantle metasomatism; fluid; peridotite

1. Introduction

The term “mantle metasomatism” [1–5] is suggested to describe the processes of transformation of mantle rocks under the influence of external fluids and/or melts, regardless of their origin and composition. Melts acting during the mantle metasomatism vary from hydrous silicic to carbonatite varieties, whereas the C–O–H fluids contain various salt components [5]. Relics of these melts and fluids are preserved as inclusions in mantle minerals, including diamonds [5–8]. The oceanic crustal material subducted to the mantle depths is traditionally considered as a major source for metasomatizing melts and fluids, enriched in H_2O , CO_2 , alkalis, halogens, etc. [6,9–13]. Their interaction with the upper mantle rocks is responsible not only for wide variability of parageneses in the mantle rocks but also for formation of specific magmas, such as kimberlites, carbonatites, lamproites, alkali basalts, kamafugites and others [14,15]. The type of mantle metasomatism producing phases, which are atypical of the peridotites and eclogites, were called by B. Harte [16] the “modal mantle metasomatism”. This process is commonly expressed in the formation of amphiboles, phlogopite, apatite, carbonates, sulfides, titanite, ilmenite, rutile, as well as a number of specific rare mineral phases enriched in Large Ion Lithophile Elements (LILE), High Field Strength Elements (HFSE), Light Rare Earth Elements (LREE), U and Th, such as hollandite (priderite), magnetoblumbite (yimengite–hawthorneite) and crichtonite (mathiasite–lindleyite) group minerals and others.

Among these phases, phlogopite is widely accepted as a major mineral indicator of the modal metasomatism in the upper mantle within a very wide P–T range and fluid/melt compositions [5]. In fact, pure phlogopite is stable up to pressure above 9 GPa and temperatures up to 1400 °C [17,18]. In

K-bearing sub-alkaline peridotite assemblages, it is stable to pressures to 6 GPa and temperatures up to 1100 °C, but phlogopite persists up to 10 GPa and higher temperatures in the peralkaline portion of the model system $K_2O-N_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O$ [19]. The assemblage diopside + phlogopite produces the K-richterite-bearing assemblages (which involve clinopyroxene containing about 1 wt. % K_2O) at pressure between 8 and 14 GPa at 1200–1350 °C [20]. Isomorphic substitutions of Ti and F notably extend phlogopite P–T stability (e.g., [21]). Because of wide P–T stability range, phlogopite is a common mineral in mantle xenoliths, especially peridotitic and pyroxenitic ones, whereas individual phlogopite inclusions are present both in eclogitic and peridotitic diamonds worldwide [22–26]. Phlogopite is found as daughter phase in high-Mg carbonatitic fluid/melt inclusions in fibrous diamonds [27] suggesting phlogopite to be an important component of the diamond growth media.

The present paper reviews data on major phlogopite-forming reactions in upper-mantle peridotites as mineral indicators of potassic modal metasomatism. The review includes both descriptions of naturally occurring reactions and results of experiments that model some of these reactions. The paper expands the approach of thermodynamic modeling of the phlogopite-forming reactions for various mantle rocks using the Gibbs free energy minimization (pseudosection method) suggested by us earlier [28].

2. Methods and Procedures

2.1. Experimental Methods

Experiments at 5 GPa, results of which are considered in this paper, were performed with a high-pressure toroidal ‘anvil-with-hole’ apparatus (a modification of the uniaxial Bridgman-type anvil apparatus). High-pressure assembly is based on a cell made of lithographic limestone and equipped with graphite heaters. Experiments were performed in hermetically sealed spherical platinum capsules (0.2 mm wall thickness) placed in cells equipped with tube graphite heaters (7.5 mm in diameter and 0.75 mm thick) and holders made of the MgO-BN mixture as the pressure medium. The cells were compressed between two WC anvils using a 4903 kN hydraulic press. Pressure at room temperature was calibrated using the phase Bi transitions at 2.55 GPa (Bi I–Bi II), 2.7 GPa and 7.7 GPa (Bi III–Bi V). The run pressure was controlled to 0.2 GPa. The experiments were not monitored directly with thermocouples, and the current power setting control of temperature was calibrated against a Pt₇₀Rh₃₀/Pt₉₄Rh₆ thermocouple without pressure correction. The run temperature was monitored using a MINITHERM-300.31 controller (Moscow Factory of Thermal Automatics, Russia). Experiments were quenched at 200–300°/s by shutting the power off and then depressurized.

2.2. Analytical Methods

Microprobe analyses of minerals in natural samples and in the experimental run products were performed using Tescan VEGA TS 5130MM (Tescan, Czech Republic) electron microscope equipped with EDS INCA Energy 450 (Oxford Instruments, UK) and Tescan VEGA-II XMU microscope (Tescan, Czech Republic) equipped with EDS INCA Energy 450 and WDS Oxford INCA Wave 700 (Oxford Instruments, UK). Analyses were performed at 20 kV accelerating voltage with a beam current up to 400 pA, spot size 115–150 nm and a zone of “excitation” with 3–4 µm diameter. Counting time was 100 s for all elements. The ZAF matrix correction was applied. The following standards were used: SiO₂ for Si, albite for Na, microcline for K, wollastonite for Ca, pure titanium for Ti, corundum for Al, pure manganese for Mn, pure iron for Fe, periclase for Mg, BaF₂ for Ba, NaCl for Cl.

2.3. PERPLE_X Calculation Strategy and Procedure

Experimental data on phlogopite-forming reactions in peridotite systems with fluid containing variable concentrations of alkali salt components (see below) show that the products of these reactions involving chloride and carbonate fluid components are generally similar. This conclusion allows qualitative comparison of these reactions and corresponding phase assemblages by constructing $\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{K}_2\text{O}})$ diagrams. Activity of K_2O in this case represents a relative scale for predicting mutual effects of the potassium activity. The standard properties of alkali components can be assumed to be the properties of K_2O and Na_2O solid oxides or melts. The calculated K_2O activities can be transformed into activities of the corresponding salt components at known activities of Cl and CO_2 . The diagrams were calculated using the Gibbs free energy minimization procedure for a system of known bulk composition using the PERPLE_X software (version 6.7.7., J.A.D. Connolly, Institut für Mineralogie und Petrographie, ETH-Zentrum, Zürich, Switzerland [29]). The standard properties of the alkali components were assumed to be those of solid K_2O and Na_2O oxides, which were compiled from the NIST thermodynamic database. Standard thermodynamic properties of endmembers from the database [30]. In contrast to previous calculations [28], which did not consider the Cr-content of minerals, in the present study we used the following models for Cr-bearing mineral solid solutions from Jennings and Holland [31]: O(JH) for olivine, Opx(JH) for orthopyroxene, Cpx(JH) for clinopyroxene, Grt(JH) for garnet and Sp(JH) for spinel. The model cAmph(G) [32], which includes K-pargasite component, was used for monoclinic amphibole. The model Bio(TCC) [33] was chosen for Ti-bearing biotite. In simulations of eclogite assemblages, the models Cpx(HP) for non-ideal disordered clinopyroxene, Gt(W) for Ca–Mg–Fe–Mn garnet [34], Pheng(HP) for dioctahedral mica, and the model “feldspar”, based on the solution model of [35], for ternary feldspar were used. The fugacity of H_2O was described by the CORK EoS [36]. Melting reactions were not taken into account because the compositions of alkaline melts in certain parts of the systems are beyond the scope of the melt models recommended in PERPLE_X under pressures above 1 GPa. For simplicity, Fe_2O_3 was not included in the calculations.

3. Phlogopite-Forming Reactions in the Upper-Mantle Rocks

3.1. Reactions in Peridotites

Phlogopite extensively forms in mantle peridotites transforming initial harzburgites and lherzolites to phlogopite wehrlites both in garnet and spinel-facies [37–47]. Xenoliths of metasomatized peridotite show various specific textures indicating major reactions forming phlogopite via interaction of the rocks with potassic fluids and melts (Figure 1a–c).

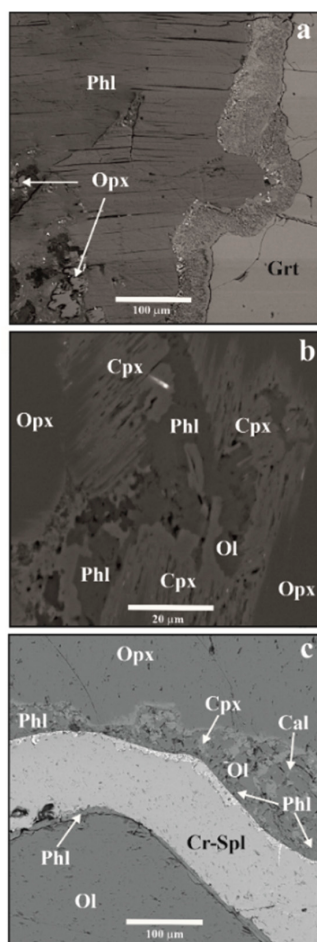
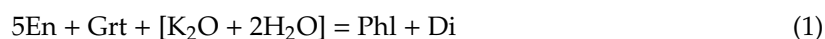
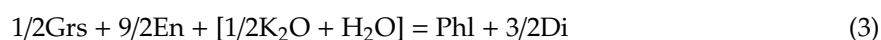
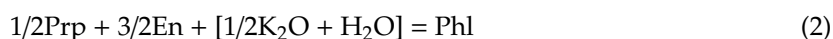


Figure 1. Phlogopite-bearing reaction textures in the metasomatized peridotite xenoliths in kimberlites of the Udachnaya pipe, Yakutia. (a) Wide phlogopite corona containing relics of orthopyroxene around garnet from the garnet peridotite; later kelyphite zone is developed between phlogopite and garnet relic. (b) Reaction zone composed of phlogopite, clinopyroxene, olivine and calcite at the contacts of orthopyroxene and Cr-spinel from the spinel harzburgite. (c) The reaction zone of “spongy” clinopyroxene, phlogopite and olivine developed on orthopyroxene in garnet lherzolite (photo courtesy of I. Sharygin, Institute of the Earth’s Crust, Siberian Branch of RAS, Irkutsk). All mineral abbreviations are from [48].

Kushiro and Aoki [49] and Aoki [50] firstly proposed the reaction:



(all mineral abbreviations in the text are from [50]), where Grt—pyrope-grossular garnet $\text{CaMg}_2\text{Al}_2\text{Si}_3\text{O}_{12}$, as the major mechanism for phlogopite formation in garnet-facies peridotites. The reaction is a combination of two end-member reactions:



which demonstrate a leading role of orthopyroxene in the phlogopite formation. Presence of Al_2O_3 as Mg-Tschermack molecule in orthopyroxene suggests the additional reaction:



In mantle peridotites, reactions (2) and (3) form phlogopite-bearing reaction textures between orthopyroxene and garnet (Figure 1a), which commonly accompanied by clinopyroxene and Cr-spinel. Aoki [49] concluded that phlogopite-rich xenoliths from kimberlites were formed from initial garnet harzburgites or orthopyroxene-rich lherzolites with increasing degree of metasomatism. For example, in xenoliths from the Lethlakane pipe, Botswana [46], this process is expressed in gradual replacement of garnet in harzburgites with the assemblage clinopyroxene + phlogopite $\pm$ Cr-spinel and decrease of the orthopyroxene mode in accordance with the reactions (1)–(3). The pseudosection $\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{K}_2\text{O}})$ in Figure 2a represents stages of metasomatic transformation exemplified by a representative composition of a garnet lherzolite corresponding to the primitive mantle composition [51] at 2 GPa and 900 °C (i.e., parameters near the continental geotherm).

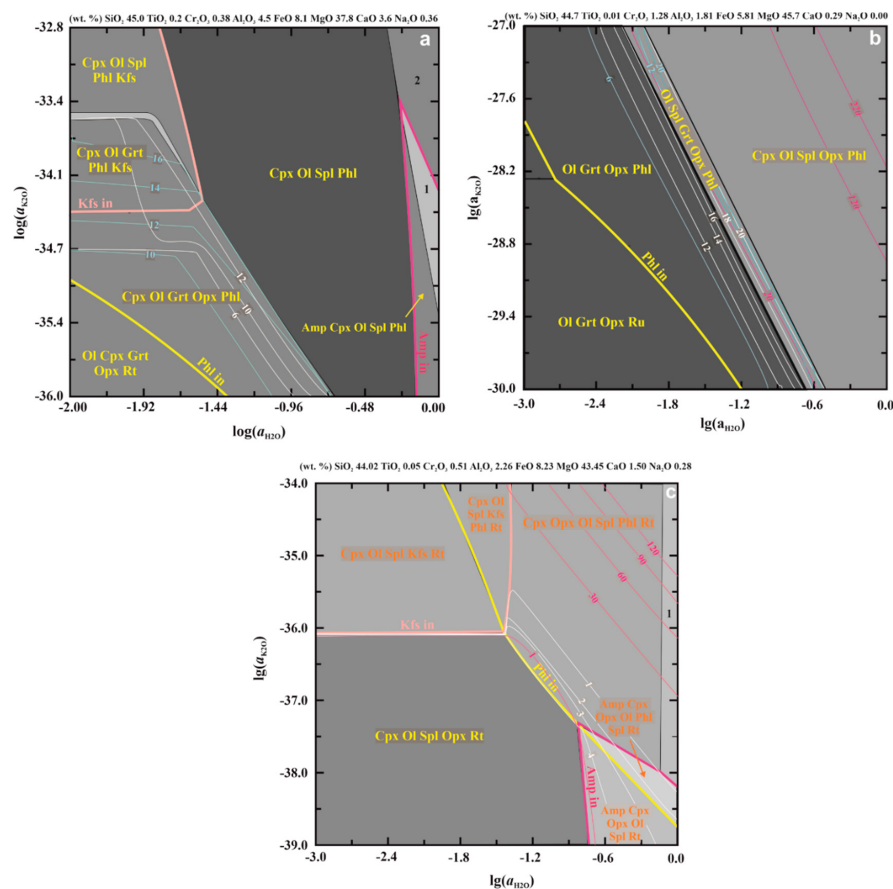
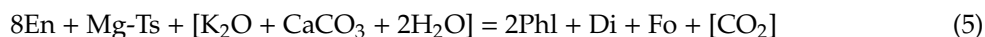


Figure 2. The $\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{K}_2\text{O}})$ pseudosections for various peridotites illustrating reactions of phlogopite formation and regularities of compositional variation of coexisting minerals in these reactions. (a) The pseudosection for the garnet lherzolite corresponding to the primitive mantle composition [51] at 2 GPa and 900 °C; white isopleths— $100\text{Cr}/(\text{Al} + \text{Cr})$ in garnet, blue isopleths— $100\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe} + \text{Mn})$ in garnet. 1—phase field Amp + Cpx + Ol + Spl + Phl, where a presence of Na-phlogopite component in mica is predicted, 2—phase field Cpx + Ol + Spl + Phl, where a presence of Na-phlogopite component in mica is predicted. (b) The pseudosection for the representative harzburgite JSL266 from the Lethlakane kimberlite pipe [46] for 4.5 GPa and 1000 °C; white isopleths— $100\text{Cr}/(\text{Al} + \text{Cr})$ in garnet, blue isopleths— $100\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe} + \text{Mn})$ in garnet, magenta isopleths— $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio in spinel. (c) The pseudosection for the spinel lherzolite from the Hamar-Daban Range, southern Siberia (sample 520-9 from [52]) at 1.8 GPa and 950 °C; white isopleths—the Al_2O_3 (wt. %) content in orthopyroxene, magenta isopleths— $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio in spinel. 1—phase field Cpx + Opx + Ol + Spl + Phl + Rt, where a presence of Na-phlogopite component in mica is predicted. All mineral abbreviations are from [48].

The slopes of phlogopite-forming reactions show that a high H_2O activity is favorable for peridotite transformation at lower K_2O activity (Figure 2a). This conclusion is qualitatively consistent with the conclusion by Sokol et al. [53,54] that K_2O concentration is negatively correlated with the $H_2O/(H_2O + CO_2)$ ratio that is required for phlogopite stabilization in peridotite. Within a narrow $\log(a_{K_2O})$, all associations of metasomatized garnet peridotite are stable, from unaltered lherzolite $Opx + Ol + Grt + Cpx + Ru$ (rutile appears since no Ti substitutions are accounted in model pyroxene, garnet and olivine solid solutions) through phlogopite-bearing garnet peridotite $Grt + Opx + Phl + Ol + Cpx$ to Cr-spinel-bearing phlogopite wehrlite $Phl + Ol + Cpx + Spl$. Spinel forms via decomposition of Cr-bearing garnet, whereas mode of clinopyroxene increases via phlogopite-forming reactions.

New clinopyroxene along with phlogopite forms in the rocks, which initially did not contain clinopyroxene, as well. To illustrate this feature, the $\log(a_{H_2O}) - \log(a_{K_2O})$ pseudosection for 4.5 GPa and 1000 °C (Figure 2b) is computed for the representative harzburgite JSL266 from the Lethlakane kimberlite pipe [46], which has not contained clinopyroxene before metasomatism. Transformation of this rock via increase of K_2O activity results in gradual disappearance of Cr-bearing garnet with partial preservation of orthopyroxene, which is a dominant phase in the initial rock. As a result, new clinopyroxene and Cr-bearing spinel form consistently with petrographic observations in the series of metasomatized xenoliths [46]. However, in some cases, new clinopyroxene does not form during garnet decomposition to phlogopite [44,47]. The pseudosection in Figure 2b demonstrates that such cases would correspond to lower $\log(a_{H_2O})$ and $\log(a_{K_2O})$ values. Such phlogopite-bearing reaction textures are usually accompanied by stronger zoning of garnet grain relics (see below).

Reaction (4) describes a formation of phlogopite directly after orthopyroxene. Phlogopite-bearing reaction textures on orthopyroxene are common feature of the metasomatized peridotites (Figure 1b). As a rule, phlogopite in them is present as inclusions and ingrowths in “spongy” clinopyroxene surrounding orthopyroxene and commonly is accompanied by secondary olivine (Figure 1b). Formation of clinopyroxene and olivine could be related to the reaction of orthopyroxene with a Ca-component of the alkalic fluid, for example, $CaCO_3$, so that the total reaction of the phlogopite formation after orthopyroxene can be written as



However, it cannot be excluded that clinopyroxene “exsolves” from initial orthopyroxene after replacement of the enstatite component by phlogopite. Reaction textures on orthopyroxene are characteristic for both garnet and spinel-facies peridotites. In spinel-facies peridotites, phlogopite-forming reactions are also result in decrease of modal contents of orthopyroxene and spinel according to reaction:

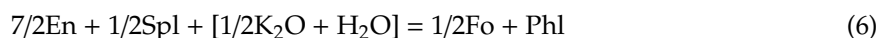


Figure 1c demonstrates the reaction texture corresponding to the reaction (6) in spinel harzburgite from the Udachanya kimberlite pipe, Yakutia. Again, phlogopite in this reaction texture is accompanied by clinopyroxene and olivine, which were formed either because of Ca-carbonate component in the fluid (calcite is present in the reaction texture) or extraction of diopside component from the starting orthopyroxene initially containing up to 0.6 wt. % CaO. Figure 2c shows mineral assemblages forming during the metasomatic transformation of spinel lherzolite at 1.8 GPa and 950 °C exemplified by a xenolith from the Hamar–Daban range, southern Siberia (sample 520-9 from [52]). In this rock all metasomatic reactions proceed after orthopyroxene. At $\log(a_{H_2O}) > -1$, phlogopite forms at the expense of orthopyroxene and Al-component of spinel via reaction (6). Although orthopyroxene remains stable with phlogopite, its Al-content significantly decreases with a progress of the phlogopite-forming reactions in correspondence with the reaction (4).

Francis [55] and Delaney et al. [56] specially paid attention that the clinopyroxene–phlogopite assemblage in peridotite xenoliths formed via break-up of primary pargasitic amphibole reflecting the following reaction:



The reaction (7) implies that relations between phlogopite and Ca–Na–amphibole are regulated by the ratio of K and Na activities in fluids, which is probably determined by fractionation of alkalis during fluid migration through the mantle rock column (e.g., [57]). The pseudosections (Figure 2a,c) demonstrate that the coexistence of phlogopite and pargasite amphibole characterizes relatively high water activity, whereas increase of potassium activity results in replacement of Ca–Na amphibole with phlogopite. Both pseudosections predict that phlogopite forming from decomposition of amphibole would be enriched in Na, i.e., in aspidolite component, $\text{Asp} = \text{NaMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. Therefore, the reaction (7) can be re-written as:



The Na_2O content in phlogopite from spinel-facies metasomatized peridotites usually varies within 0.1–0.7 wt. % (e.g., [46,47,49,57]), but in some cases reaches 1.5 wt. %. Various authors [55,58] explain this compositional feature of phlogopite by metasomatic processes induced by Na-rich fluid. In this case, the K/Na ratio of phlogopite serves as an indicator of the K/Na ratio of the fluid. In addition, this ratio can be an indicator of initial Na content in the reacting fluid/melt, as well as temperature, since the phlogopite/melt (and, probably, fluid) Na partitioning coefficient decreases with cooling [10]. However, present calculations show that Na-component in phlogopite can be produced from transformation of hydrous amphibole-bearing peridotite at pressures below 2.5 GPa, i.e., below the probable baric stability limit of aspidolite [59].

Phlogopite-forming reactions in peridotites are commonly accompanied by compositional changes of primary minerals. Various authors [37,41–46,49,55,56] note re-crystallization of clinopyroxenes and olivine with formation of new generations of these minerals along with phlogopite. New clinopyroxene is usually depleted in Na_2O and Al_2O_3 implying a participation of jadeite and Ca-Tschermack components in the phlogopite-forming reactions.

There are various tendencies in variation of garnet composition in a progress of phlogopite-forming reactions. Schulze [43] and Griffin et al. [44] noted that formation of phlogopite reaction rims around garnet resulted in their zoning with respect to both major and trace elements. In garnets from harzburgite xenoliths from the Wesselton kimberlites, South Africa [44], CaO increases, MgO and Cr_2O_3 decrease from cores to rims, contacting to phlogopite–Cr-spinel reaction textures. Garnet rims are enriched in Y, Zr, Ti suggesting extensive metasomatic influence. Overall, composition of garnets changes from harzburgitic cores to lherzolitic rims. In order to characterize compositional variations in minerals in the course of the phlogopite-forming reactions, isopleths in the pseudosections were plotted (Figure 2a,b). In both cases (primitive lherzolite and depleted harzburgite), the pseudosections predict a significant increase of grossular content in garnet. The rimward increase of the grossular in garnet at the phlogopite reaction rims is consistent with observation by [43,44] and implies a domination of the reaction (2) over reaction (3). In fact, secondary clinopyroxene has not been described in the phlogopite reaction rims around garnet from the xenoliths studied by Griffin et al. [44]. Following to Figure 2b, metasomatic transformations in these xenoliths seemed to occur within the garnet stability field ($\text{Ol} + \text{Spl} + \text{Grt} + \text{Opx} + \text{Phl}$) in terms of K_2O and H_2O activities. The pseudosection also demonstrates a concomitant increase of Cr_2O_3 -content in garnet in the course of phlogopite formation. In contrast, Griffin et al. [44] noted a slight, just about 1 wt. %, decrease of Cr_2O_3 during the phlogopite-forming reactions in number of harzburgite xenoliths from the Wesselton kimberlites. The inconsistency between observations from the natural assemblages and modeling results can be explained by the following reasons. The phlogopite solid solution model, which is used in the present calculations,

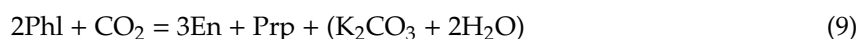
does not account for the Cr incorporation. In natural systems, phlogopite usually contains Cr₂O₃ (0.3–1 wt. %), probably, influencing on the Cr-content in coexisting garnet. In addition, garnet at contacts with phlogopite reaction textures shows a significant (up to 0.5 wt. %) increase of TiO₂ substituting Cr₂O₃. However, solubility of Ti in garnet is not accounted in the garnet solid solution model in the present calculations, as well.

In contrast to the observations by Schulze [43] and Griffin et al. [44] on garnet zoning, van Achterbergh et al. [46] found that garnets from the phlogopite-bearing harzburgites from the Lethlakane pipe were generally homogeneous in composition, and zoning in most cases is absent. Both Cr-spinel and clinopyroxene are present in the phlogopite reaction textures in these xenoliths. Taking these observations into account and following to Figure 2b, metasomatic transformations in these rocks proceeded beyond the garnet stability field at higher K₂O and/or H₂O activities, i.e., in the field Cpx + Ol + Spl + Opx + Phl.

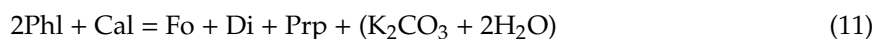
Formation of phlogopite after Cr-bearing garnet produces Cr-rich spinel as illustrated in the diagrams of Figure 2a,b. The position of isopleths shows that the Cr₂O₃/Al₂O₃ ratio of newly formed spinel rapidly increases along with its mode with a progress of phlogopite formation via increase of log(*a*_{K₂O}) and/or log(*a*_{H₂O}) (Figure 2b). As an illustration for this rule, van Achterbergh et al. [46] noted that phlogopite wehrlites, which represent the highest degree of metasomatic transformation of garnet harzburgites, contain the most Cr-rich spinel. Similar increase of the Cr₂O₃/Al₂O₃ ratio of spinel occurs via phlogopite-formation on the spinel-facies lherzolite as well (Figure 2c). Figure 1c shows rims of Cr-rich spinel around the primary spinel at the contacts with the phlogopite–clinopyroxene–olivine reaction textures developed after the simultaneously operating reactions (4)–(6). Figure 2c indicates that phlogopite-forming reactions produce the strongest variations in mineral composition both garnet and spinel-facies peridotites.

3.2. Experimental Studies of Phlogopite-Forming Reactions in Peridotites

The above regularities in the phlogopite-forming reactions are supported by experiments on interaction of peridotite assemblages with potassic fluids of different anionic composition. Safonov and Butvina [60] studied interaction of a model peridotite in the Na₂O-bearing CMAS system at 1.9 ГПа and 900–1200 °C with H₂O–KCl fluids with variable H₂O/KCl ratio. They revealed that formation of phlogopite, clinopyroxene and, probably, olivine actively proceeded after decomposition of aluminous orthopyroxene, garnet, spinel and pargasite amphibole, encompassing all spectrum of the above reactions. Authors mention that instability of orthopyroxene with Al-rich phases in presence of potassic fluids is a major factor of phlogopite formation within a wide range of fluid composition. Edgar and Arima [61] and Thibault and Edgar [62] noted that phlogopite growth was accompanied by regular decrease of the orthopyroxene/clinopyroxene and orthopyroxene/olivine ratios, rapid disappearance of pargasite and spinel at 2 GPa and garnet at 3 GPa during interaction of a model peridotite with the H₂O–K₂CO₃ fluids containing up to 80 wt. % carbonate. Phlogopite is found to be the only K-bearing crystalline phase in these experiments. However, the situation is more complex at higher pressures. Ulmer and Sweeney [63] revealed that phlogopite was unstable in presence of hydrous carbonate–silicate liquid simulating Group II kimberlites at >4 GPa and >1150 °C and suggested reactions:



as limiting phlogopite-out mechanisms in CO₂ and carbonate-bearing systems. Sokol et al. [52,53] added a reaction



as a mechanism of disappearance of phlogopite at 5.5–7.0 GPa at 1200–1350 °C. They showed that at constant $\text{H}_2\text{O}/(\text{CO}_2 + \text{H}_2\text{O})$ ratio 0.35–0.40, phlogopite formed in the system with a bulk K_2O content above 11 wt. %, whereas K-carbonates were stable at K_2O 3–4 wt. %. Along with other data [63–66], these results indicate that stabilization of phlogopite with respect to K-carbonate in systems with high X_{CO_2} requires higher K_2O . This conclusion can be generalized: The lower H_2O activity in a fluid equilibrated with peridotite, the higher K_2O activities are necessary for the phlogopite formation. This conclusion is visualized in $\log(a_{\text{H}_2\text{O}}) - \log(a_{\text{K}_2\text{O}})$ pseudosections for peridotites, where the phlogopite-in reaction lines show a negative slope (Figure 2a–c).

Pseudosection modeling shows that olivine mode remains constant or just slightly decreases (by 3–4 vol. %) in the course of the phlogopite-forming reactions. Thus, olivine is not actively consumed during the formation of phlogopite in the peridotite assemblages. Phlogopite-bearing reaction textures in mantle xenoliths indicate a passive role of primary olivine and formation of new generations of olivine via reaction like (5) and (6). Passive role of olivine in the phlogopite-forming reactions is proved by the experiments [60–62]. Nevertheless, olivine can be a reactant phase in the phlogopite-forming reaction during interaction of peridotite with alkalic silicate melts. It has been recently demonstrated in the experiments on interaction of dunite with alkalic sediment-derived melts and hydrous basanitic melts, modeling processes a fore-arc subduction and postcollisional rifting environments, respectively [10].

None of the above experimental studies reported variations of compositions of phases coexisting with phlogopite. In order to do it, experiments on the systems enstatite–pyrope–grossular and enstatite–pyrope–knorringite in presence of H_2O –KCl fluids with variable $\text{H}_2\text{O}/\text{KCl}$ ratio were performed at 5 GPa. These experiments were aimed at the tracing of variations of grossular and knorringite contents in garnet with variations of the KCl content in the fluid. Study of the reactions (2) and (3) in the system enstatite–pyrope–grossular at 5 GPa and 1000 °C shows that phlogopite actively forms at the KCl content 5–10 mol. % in the fluid. At these conditions, phlogopite coexists with both pyroxenes and garnet. Increase of the KCl content in the fluid results in gradual disappearance of garnet and orthopyroxene and stronger domination of phlogopite and clinopyroxene (Figure 3).

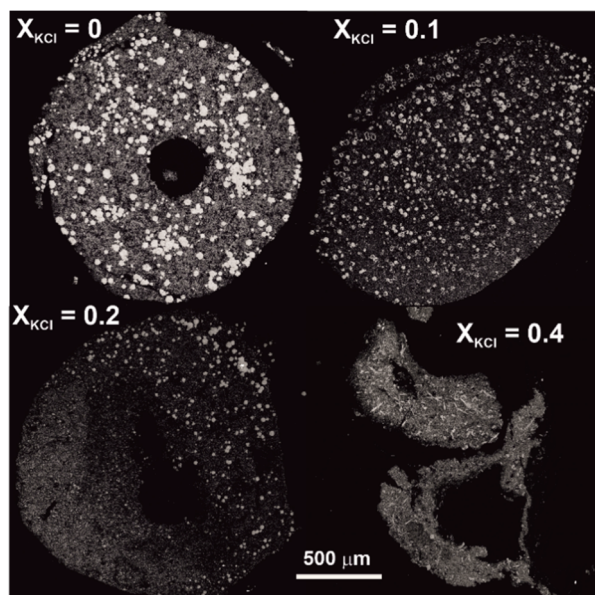


Figure 3. BSE images of the run samples in the system enstatite–pyrope–grossular illustrating a gradual transformation of the garnet–two pyroxene assemblage ($X_{\text{KCl}} = 0$) to clinopyroxene–phlogopite assemblage ($X_{\text{KCl}} = 0.4$) with the increasing KCl content in the aqueous–salt fluid at 5 GPa and 1000 °C. The presence of silicate melt in the run products is not excluded.

Therefore, at 40 mol. % of KCl in the fluid, phlogopite and clinopyroxene only are present in the run products. Phase compositions regularly vary with the increase of the salt content in the fluid (Figure 4a,b). The Al-content of orthopyroxene decreases in correspondence with the reaction (4) (Figure 4a). Grossular content in garnet increases with the increase of the KCl concentration in the fluid up to 10 mol. % demonstrating a domination of the reaction (2) over the reaction (3) (Figure 4b). However, further increase of the KCl concentration up to 20 mol. %, the grossular content in garnet decreases reflecting simultaneous operation of these reactions (Figure 4b).

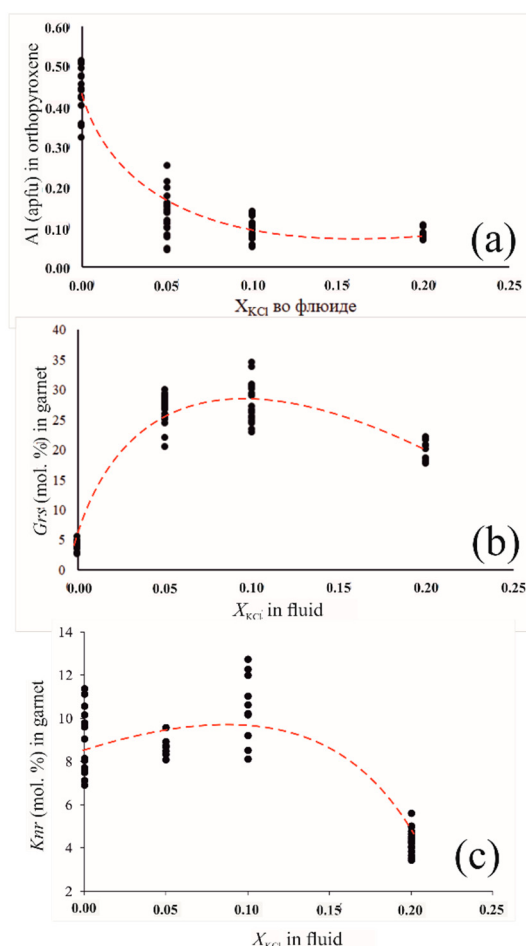


Figure 4. Dependence of phase compositions in the systems enstatite–pyrope–grossular–H₂O–KCl and enstatite–pyrope–knorringite–H₂O–KCl on the salt concentration in a fluid at 5 GPa. (a) Al in orthopyroxene (atoms per formula unit, apfu); (b) grossular in garnet (mol. %); (c) knorringite in garnet (mol. %).

In the system enstatite–pyrope–knorringite at the KCl content in the fluid 0–10 mol. %, garnet contains 3.0–3.6 wt. % Cr₂O₃ (8–9 mol. % of knorringite). Cr-bearing phlogopite (about 2 wt. % Cr₂O₃) appears in this system at 10 mol. % KCl in the fluid, and its formation results in tendency for a slight increase of the knorringite content in garnet (Figure 4c). Cr-bearing spinel does not form in the system enstatite–pyrope–knorringite because of relatively high SiO₂ bulk content in comparison to the typical peridotite. Nevertheless, at 20 mol. % KCl in the fluid, kyanite with up to 7 wt. % Cr₂O₃ appears in the run products resulting in a decrease of the Cr₂O₃ content in garnet down to 1.7–1.8 wt. %, i.e., 3–5 mol. % of knorringite (Figure 4c). The Cr₂O₃ content in the coexisting phlogopite also decreases by about 1 wt. %.

Thus, the above experiments allowed reproduction of some characteristic regularities in variations of garnet and pyroxene compositions in the course of phlogopite formation in peridotites. These effects

can be applied for the quantitative and qualitative estimates of variations in K activity during the modal mantle metasomatism as illustrated by the $\log(a_{K_2O}) - \log(a_{H_2O})$ pseudosections (Figure 2a–c).

3.3. Relation of Phlogopite with Other Potassic Phases in the Metasomatized Upper-Mantle Rocks

Reaction textures indicating instability of phlogopite with respect to other K-bearing phases are rarely reported in both peridotite and eclogite xenoliths. However, in the metasomatized xenoliths, phlogopite coexists or is associated with a number of other potassic phases, which can be competing to phlogopite as indicators of potassium and water activities during mantle metasomatism.

K-richterite, $(K, Na)^A Na^{M4} Ca^{M4} Mg_5 Si_8 O_{22} (OH)_2$, is a typical amphibole coexisting with phlogopite in xenoliths of the MARID (mica–amphibole–rutile–ilmenite–diopside) suite [67], strongly metasomatized phlogopite–K-richterite peridotites, so called PKP [68], and garnet-free phlogopite–diopside veins in peridotite xenoliths [39,40]. According to experimental studies [19,69–72], the assemblage garnet + K-richterite is unstable at pressures below 6–7 GPa with respect to the assemblage clinopyroxene + phlogopite $\pm$ orthopyroxene because of reaction:



suggesting that the K-richterite forms at depths greater than ~200 km. However, the leading factor that stabilizes K-richterite is a potassium content (activity) in the mantle systems. K-richterite along with phlogopite easily crystallizes in the peralkaline, i.e., with molar $(Na_2O + K_2O)/Al_2O_3 > 1$, systems [19,71,72]. The MARID suite is the best example of peralkaline mantle assemblages. The peralkaline assemblages related to metasomatism are PKP, i.e., phlogopite–K-richterite peridotites [39,46], which are products of a progressive replacement of garnet by phlogopite and eventually by K-richterite so that garnet peridotites are succeeded by garnet–phlogopite peridotites (GPP), garnet-free phlogopite peridotites (PP) and, ultimately, by PKP. These observations indicate that K-richterite is a product of higher degree of metasomatism corresponding to the higher K (and Na) activities than it is needed for the phlogopite. At these conditions, Al is predominantly accommodated by phlogopite, and K starts to be bound to Ca and Si in amphibole. However, there is no reports for phlogopite replacement by K-richterite in metasomatized peridotites. Both minerals form jointly at advanced stages of metasomatism at the expense of pyroxenes, Cr-spinel and other minerals, which survived initial stages of metasomatism.

Another competing phase for phlogopite in mantle assemblages can be sanidine, $KAlSi_3O_8$, since its stability extends to pressures 5.5–7 GPa at 1000–1600 °C [73,74]. There are numerous reports on sanidine inclusions in diamonds, which belong to eclogite paragenesis [22,75–81]. The close association of sanidine with eclogite parageneses is supported by findings of this phase in eclogite xenoliths including coesite and kyanite varieties and grossspidites [82–85], as well as in products of metasomatic modifications of eclogites [86–88]. Findings of sanidine in peridotite assemblages are unique. “Mixed assemblage” of sanidine with Fe-enriched olivine is reported only in diamond from the Shengli-1 kimberlite pipe, China [89]. Both in H_2O -free conditions and in presence of H_2O or H_2O – CO_2 fluids, sanidine is not stable with Mg-rich olivine at pressures above 1.5–2.5 GPa but can coexist with phlogopite at pressures below 2.5 GPa [90] compatible to off-cratonic spinel-facies peridotites only. As an example, feldspar with 50–60 mol. % of sanidine was described in spinel peridotites xenoliths from number of alkali basalt occurrences (see references in [91]). In all rocks, feldspar forms fine-grained aggregates with olivine, Ti-oxides and Cr-spinel between corroded primary spinel and orthopyroxene suggesting a reaction, which is similar to phlogopite-forming reaction (6). However, in many cases, these reaction textures are not accompanied by phlogopite (or amphibole). Moreover, there are textural evidences for replacement of phlogopite by feldspar-bearing aggregates [91]. These textures features suggest an extremely low H_2O activity in a fluid, which interacted with peridotite at temperatures 950–1000 °C and pressures below 2 GPa. The pseudosection $\log(a_{H_2O}) - \log(a_{K_2O})$ for the spinel lherzolite from the Hamar–Daban Range, southern Siberia (sample 520-9 in [52]), demonstrates

that $\log a_{\text{H}_2\text{O}} < -1.5$ is needed to produce feldspar-bearing assemblage in this peridotite (Figure 2c). This result is roughly consistent with the experimental data on the peridotite–H₂O–CO₂ systems at pressures below 1.5 GPa, showing a possibility of subsolidus phlogopite decomposition to form K-feldspar at X_{CO_2} above 0.8 [92]. The pseudosection for lherzolite (Figure 2c) demonstrates that K-feldspar generally forms at the K₂O-activities higher than it is needed for phlogopite formation. Thus, appearance of K-feldspar instead of phlogopite in peridotite assemblages manifests an unusual condition of extremely low water activity, which can be attributed, probably, to water-poor alkalic carbonatite or carbonate–salt liquids interacting with mantle rocks.

In strongly metasomatized peridotite xenoliths from kimberlites, phlogopite commonly coexists with various rare K–Ba-bearing phases, such as hawthorneite–yimengite, HAWYI (K, Ba)(Cr, Ti, Mg, Fe, Al)₁₂O₁₉, lindsleyite–mathiasite, LIMA (K, Ba)(Cr, Ti, Mg, Fe, Al)₂₁O₃₈, priderite, (K, Ba)_{1–2}(Cr, Ti, Mg, Fe, Al)_{6–7}O₁₆ and other more rare phases [93]. Experimental data on synthesis of K–Ba-titanates demonstrate that there are virtually no restrictions on their stability in the upper-mantle [94,95] confirming the possibility of coexistence of these phases with diamond in the subcontinent upper mantle in the regions of generation of kimberlites and lamproites. It is evident that specific chemical conditions are responsible for the stability of K–Ba-titanates along with phlogopite. Phlogopite is not only active container of K and other LILE, but also is able to accommodate Cr and Ti. Thus, phlogopite acts as contender for K–Ba-titanates. Thus, these minerals form when the ability to concentrate K and LILE in phlogopite (and K-richterite) is exhausted manifesting the highest degree of metasomatic changes in the conditions of high activity of alkaline components in fluids (melts) with low SiO₂ activity [96,97].

Figure 5 shows coexisting phlogopite and K-titanates (mathiasite and priderite) in the products of experiments on interaction of chromite + ilmenite (rutile) with H₂O–CO₂–K₂CO₃ fluids at 5 GPa and 1200 °C [98].

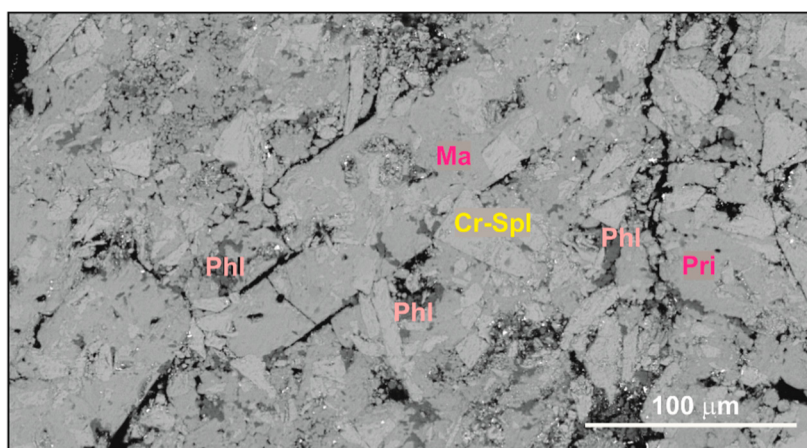


Figure 5. Phlogopite coexisting with mathiasite and priderite in the run products of interaction of Cr-bearing spinel and rutile with the fluid H₂O–CO₂–K₂CO₃ at 5 GPa [98]. Ma—mathiasite, Pri—priderite, all other mineral abbreviations are from [48].

Phlogopite was formed in these experiments due to a presence of silicate phases included or intergrown with starting natural ilmenite and chromite. It contains 0.6–1.9 wt. % TiO₂ and 1.8–2.7 wt. % Cr₂O₃, reflecting formation via the reactions involving both chromite and Ti-phases. The highest concentrations of Ti and Cr are detected in phlogopites forming in the reactions with fluids with high K₂CO₃/(H₂O + CO₂) ratios suggesting more active involvement of chromite and ilmenite with the potassium-rich fluids forming both Cr-bearing K-titanates and phlogopite. However, phlogopite is present even in run products, which do not contain titanates. These experiments are characterized by the lowest K₂CO₃/(H₂O + CO₂) ratios in the starting fluid mixture. This means that the crystallization of K-titanates together with phlogopite is determined exclusively by the K activity of a fluid, which

corresponds to the highest degrees of metasomatism. Such conditions can be created either with a continuous interaction of ultrapotassic fluids/melts with rocks or during a multi-stage process with an increasing effect. For example, two-stage metasomatic process is described by Konzett et al. [96] in the spinel harzburgites from kimberlites of South Africa. The first stage of metasomatic transformation results in the formation of phlogopite, K-amphibole, titaniferous phase (rutile and srilankite) and mathiasite. The subsequent stage of metasomatism is manifested by the decomposition of these minerals to form new generations of phlogopite, clinopyroxene, olivine, various rare Ti and Zr-bearing minerals, as well as replacement of mathiasite with Cr-rich priderite. The authors believe that the second stage of metasomatism was due to the interaction of rocks with ultra-alkaline fluids/melts with low silica activity [96], which is typical for alkaline carbonatite melts. Reactions of phlogopite with relic Cr-rich spinel can form K-bearing titanates at the advanced stage of metasomatic processes (e.g., [99]). However, such reactions have never been modeled experimentally.

Interaction of K-rich (and Cl-bearing) fluid/melts or percolating kimberlite melts with mantle rocks containing primary Fe–Cu–Ni sulfides results in formation of K-bearing sulfides, among which djerfisherite, $K_6(Fe,Ni,Cu)_{25}S_{26}Cl$ (see review and references in [100]) is the most common mineral. Djerfisherite typically occurs both as replacement rims on pre-existing pyrrhotite, pentlandite or chalcopyrite and as individual interstitial grains in mantle xenoliths. Its P–T stability at mantle conditions is extremely poorly constrained (e.g., [101]). However, it is evident that the djerfisherite stability is highly dependent on a presence of a K-chloride component, which affects water activity and, thus, determines formation of coexisting phlogopite. In fact, in mantle xenoliths, djerfisherite occurs both in association with phlogopite and without phlogopite [100]. No textures indicating reaction relationships between djerfisherite and phlogopite were reported from xenoliths.

4. Conclusions

The above review from natural assemblages shows that there were no alternative for phlogopite as a leading potassic phase during mantle metasomatism within a wide interval of rock bulk composition, pressure, temperature, water and alkali activity. Phlogopite-forming reactions can be potentially utilized as indicators of K and water activities in fluid acting during metasomatism in the upper mantle. They indicate that K activity is extremely important intense parameter of the evolution of mantle mineral systems and, hence, cannot be ignored in the study of mantle metasomatism. The phlogopite-forming reactions governed by K activity and the corresponding mineral assemblages can be adequately predicted based on thermodynamic modeling using the Gibbs free energy minimization in terms of the $\log(a_{H_2O}) - \log(a_{K_2O})$ diagrams. If experimental data on the dependences of these reactions on the K activity in the fluids of variable composition are available, simulations of this type enable prediction of the composition of the metasomatizing fluids and melts.

Author Contributions: O.S. suggested a conceptual basis for the paper; V.B. and E.L. produced experimental data; O.S. computed the PERPLE_X diagrams; O.S., V.B. and E.L. discussed the results, wrote the paper and prepared the figures.

Funding: The work was financially supported by the governmental projects AAAA-A18-118020590148-3 and AAAA-A18-118020590140-7 of the D.S. Korzhinskii Institute of Experimental Mineralogy.

Acknowledgments: Authors thank three anonymous reviewers for their constructive suggestions.

Conflicts of Interest: The authors declare no conflict of interests.

References

1. Lloyd, F.E.; Bailey, D.K. Light element metasomatism of the continental mantle: The evidence and the consequences. *Phys. Chem. Earth* **1975**, *9*, 389–416. [[CrossRef](#)]
2. Bailey, D.K. Mantle metasomatism—Continued chemical change within the earth. *Nature* **1982**, *296*, 525–580. [[CrossRef](#)]

3. Bailey, D.K. Mantle metasomatism—Perspective and prospect. In *Alkaline Igneous Rocks*; Fitton, J.G., Upton, B.G.J., Eds.; Geological Society Special Publication: London, UK, 1987; Volume 30, pp. 1–13.
4. Menzies, M.A.; Hawkesworth, C.J. *Mantle Metasomatism*; Academic Press: London, UK, 1987; p. 472.
5. O'Reilly, S.Y.; Griffin, W.L. Mantle metasomatism. In *Metasomatism and the Chemical Transformation of Rock*; Harlov, D.E., Austerheim, H., Eds.; Springer: Berlin/Heidelberg, Germany, 2013; pp. 471–533.
6. Weiss, Y.; McNeill, J.; Pearson, D.G.; Nowell, G.M.; Ottley, C.J. Highly saline fluids from a subducting slab as the source for fluid-rich diamonds. *Nature* **2015**, *524*, 339. [[CrossRef](#)] [[PubMed](#)]
7. Schiano, P.; Clocchiatti, R. Worldwide occurrence of silica-rich melts in sub-continental and sub-oceanic mantle minerals. *Nature* **1994**, *368*, 621–624. [[CrossRef](#)]
8. Golovin, A.V.; Sharygin, I.S.; Kamenetsky, V.S.; Korsakov, A.V.; Yaxley, G.M. Alkali-carbonate melts from the base of cratonic lithospheric mantle: Links to kimberlites. *Chem. Geol.* **2018**, *483*, 261–274. [[CrossRef](#)]
9. Förster, M.W.; Foley, S.F.; Marschall, H.R.; Alard, O.; Buhre, S. Melting of sediments in the deep mantle produces saline fluid inclusions in diamonds. *Sci. Adv.* **2019**, *5*, eaau2620. [[CrossRef](#)]
10. Förster, M.W.; Prelević, D.; Buhre, S.; Mertz-Kraus, R.; Foley, S.F. An experimental study of the role of partial melts of sediments versus mantle melts in the sources of potassic magmatism. *J. Asian Earth Sci.* **2019**, *177*, 76–88. [[CrossRef](#)]
11. Grassi, D.; Schmidt, M.W. Melting of carbonated pelites at 8–13 GPa: Generating K-rich carbonatites for mantle metasomatism. *Contrib. Mineral. Petrol.* **2011**, *162*, 169–191. [[CrossRef](#)]
12. Thomsen, T.B.; Schmidt, M.W. Melting of carbonated pelites at 2.5–5.0 GPa, silicate–carbonatite liquid immiscibility, and potassium–carbon metasomatism of the mantle. *Earth Planet. Sci. Lett.* **2008**, *267*, 17–31. [[CrossRef](#)]
13. Perchuk, A.L.; Serdyuk, A.A.; Zinovieva, N.G. Subduction Sediment–Lherzolite Interaction at 2.9 GPa: Effects of Metasomatism and Partial Melting. *Petrology* **2019**, *27*, 467–488. [[CrossRef](#)]
14. Gupta, A.K.; Fyfe, W.S. *The Young Potassic Rocks*; Ane Books: New Delhi, India, 2003; p. 370.
15. Gupta, A.K. *Origin of Potassium-Rich Silica-Deficient Igneous Rocks*; Springer: New Delhi, India, 2015; p. 536.
16. Harte, B. Mantle peridotites and processes—The kimberlite sample. In *Continental Basalts and Mantle Xenoliths*; Hawkesworth, C.J., Norry, M.J., Eds.; Shiva: Cheshire, UK, 1983; pp. 46–91.
17. Yoder, H.S.; Kushiro, I. Melting of a hydrous phase: Phlogopite. *Am. J. Sci.* **1969**, *267*, 558–582.
18. Trønnes, R.G. Stability range and decomposition of potassic richterite and phlogopite end members at 5–15 GPa. *Mineral. Petrol.* **2002**, *74*, 129–148. [[CrossRef](#)]
19. Konzett, J.; Fei, Y. Transport and storage of potassium in the Earth's upper mantle and transition zone: An experimental study to 23 GPa in simplified and natural bulk compositions. *J. Petrol.* **2000**, *41*, 583–603. [[CrossRef](#)]
20. Luth, R.W. Experimental study of the system phlogopite–diopside from 3.5 to 17 GPa. *Am. Mineral.* **1997**, *82*, 1198–1209. [[CrossRef](#)]
21. Trønnes, R.G.; Edgar, A.D.; Arima, M. A high pressure-high temperature study of TiO₂ solubility in Mg-rich phlogopite: Implications to phlogopite chemistry. *Geochim. Cosmochim. Acta* **1985**, *49*, 2323–2329. [[CrossRef](#)]
22. Prinz, M.; Manson, D.V.; Hlava, P.F.; Keil, K. Inclusions in diamonds: Garnet lherzolite and eclogite assemblages. In *Physics and Chemistry of the Earth*; Elsevier: Amsterdam, The Netherlands, 1975; pp. 797–815.
23. Sobolev, N.V.; Kaminsky, F.V.; Griffin, W.L.; Yefimova, E.S.; Win, T.T.; Ryan, C.G.; Botkunov, A.I. Mineral inclusions in diamonds from the Sputnik kimberlite pipe, Yakutia. *Lithos* **1997**, *39*, 135–157. [[CrossRef](#)]
24. Sobolev, N.V.; Yefimova, E.S.; Channer, D.D.; Anderson, P.F.N.; Barron, K.M. Unusual upper mantle beneath Guianamo, Guyana Shield, Venezuela: Evidence from diamond inclusions. *Geology* **1998**, *26*, 971–974. [[CrossRef](#)]
25. Sobolev, N.V.; Logvinova, A.M.; Efimova, E.S. Syngenetic phlogopite inclusions in kimberlite-hosted diamonds: Implications for role of volatiles in diamond formation. *Russ. Geol. Geophys.* **2009**, *50*, 1234–1248. [[CrossRef](#)]
26. Leost, I.; Stachel, T.; Brey, G.P.; Harris, J.W.; Ryabchikov, I.D. Diamond formation and source carbonation: Mineral associations in diamonds from Namibia. *Contrib. Mineral. Petrol.* **2003**, *145*, 15–24. [[CrossRef](#)]
27. Logvinova, A.M.; Zedgenizov, D.A.; Wirth, R. Specific multiphase assemblages of carbonatitic and Al-rich silicic diamond-forming fluids/melts: TEM observation of microinclusions in cuboid diamonds from the placers of Northeastern Siberian Craton. *Minerals* **2019**, *9*, 50. [[CrossRef](#)]

28. Safonov, O.G.; Butvina, V.G. Indicator reactions of K and Na activities in the upper mantle: Natural mineral assemblages, experimental data, and thermodynamic modeling. *Geochem. Intern.* **2016**, *54*, 858–872. [[CrossRef](#)]
29. Connolly, J.A.D. Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decarbonation. *Earth Planet. Sci. Lett.* **2005**, *236*, 524–541. [[CrossRef](#)]
30. Holland, T.J.B.; Powell, R. An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *J. Metamorph. Geol.* **2011**, *29*, 333–383.
31. Jennings, E.S.; Holland, T.J. A simple thermodynamic model for melting of peridotite in the system NCFMASOCr. *J. Petrol.* **2015**, *56*, 869–892. [[CrossRef](#)]
32. Green, E.C.R.; White, R.W.; Diener, J.F.A.; Powell, R.; Holland, T.J.B.; Palin, R.M. Activity–composition relations for the calculation of partial melting equilibria in metabasic rocks. *J. Metamorph. Geol.* **2016**, *34*, 845–869. [[CrossRef](#)]
33. Tajčmanová, L.; Connolly, J.A.D.; Cesare, B. A thermodynamic model for titanium and ferric iron solution in biotite. *J. Metamorph. Geol.* **2009**, *27*, 153–165. [[CrossRef](#)]
34. White, R.W.; Powell, R.; Holland, T.J.B.; Johnson, T.E.; Green, E.C.R. New mineral activity–composition relations for thermodynamic calculations in metapelitic systems. *J. Metamorph. Geol.* **2014**, *32*, 261–286. [[CrossRef](#)]
35. Fuhrman, M.L.; Lindsley, D.H. Ternary-feldspar modeling and thermometry. *Am. Mineral.* **1988**, *73*, 201–215.
36. Holland, T.J.B.; Powell, R. COmpensated Redlich-Kwong (CORK) fugacity equations for H₂O and CO₂. *Contrib. Mineral. Petrol.* **1991**, *109*, 265–273. [[CrossRef](#)]
37. Carswell, D.A. Primary and secondary phlogopites and clinopyroxenes in garnet lherzolite xenoliths. *Phys. Chem. Earth.* **1975**, *9*, 417–429. [[CrossRef](#)]
38. Jones, A.P.; Smith, J.V.; Dawson, J.B. Mantle metasomatism in 14 veined peridotites from Bultfontein Mine, South Africa. *J. Geol.* **1982**, *90*, 435–453. [[CrossRef](#)]
39. Erlank, A.J.; Waters, F.G.; Hawkesworth, C.J.; Haggerty, S.E.; Allsopp, H.L.; Rickard, R.S.; Menzies, M.A. Evidence for mantle metasomatism in peridotite nodules from the Kimberley pipes, South Africa. In *Mantle Metasomatism*; Menzies, M.A., Hawkesworth, C.J., Eds.; Academic Press: London, UK, 1987; pp. 221–311.
40. Waters, F.G.; Erlank, A.J. Assessment of the vertical extent and distribution of mantle metasomatism below Kimberley, South Africa. *J. Petrol.* **1988**, 185–204. [[CrossRef](#)]
41. Canil, D.; Scarfe, C.M. Origin of phlogopite in mantle xenoliths from Kostal Lake, Wells Gray Park, British Columbia. *J. Petrol.* **1989**, *30*, 1159–1179. [[CrossRef](#)]
42. Lloyd, F.E.; Edgar, A.D.; Forsyth, D.M.; Barnett, R.L. The paragenesis of upper-mantle xenoliths from the Quaternary volcanics south-east of Gees, West Eifel, Germany. *Mineral. Mag.* **1991**, *55*, 95–112. [[CrossRef](#)]
43. Schulze, D.J. Low-Ca garnet harzburgites from Kimberley, South Africa: Abundance and bearing on the structure and evolution of the lithosphere. *J. Geophys. Res. Solid Earth* **1995**, *100*, 12513–12526. [[CrossRef](#)]
44. Griffin, W.L.; Shee, S.R.; Ryan, C.G.; Win, T.T.; Wyatt, B.A. Harzburgite to lherzolite and back again: Metasomatic processes in ultramafic xenoliths from the Wesselton kimberlite, Kimberley, South Africa. *Contrib. Mineral. Petrol.* **1999**, *134*, 232–250. [[CrossRef](#)]
45. Konzett, J.; Armstrong, R.A.; Günther, D. Modal metasomatism in the Kaapvaal craton lithosphere: Constraints on timing and genesis from U–Pb zircon dating of metasomatized peridotites and MARID-type xenoliths. *Contrib. Mineral. Petrol.* **2000**, *139*, 704–719. [[CrossRef](#)]
46. van Achterbergh, E.; Griffin, W.L.; Stiefenhofer, J. Metasomatism in mantle xenoliths from the Letlhakane kimberlites: Estimation of element fluxes. *Contrib. Mineral. Petrol.* **2001**, *141*, 397–414. [[CrossRef](#)]
47. Kargin, A.V.; Sazonova, L.V.; Nosova, A.A.; Lebedeva, N.M.; Kostitsyn, Y.A.; Kovalchuk, E.V.; Tretyachenko, V.V.; Tikhomirova, Y.S. Phlogopite in mantle xenoliths and kimberlite from the Grib pipe, Arkhangelsk province, Russia: Evidence for multi-stage mantle metasomatism and origin of phlogopite in kimberlite. *Geosci. Front.* **2019**, *10*, 1941–1959. [[CrossRef](#)]
48. Whitney, D.L.; Evans, B.W. Abbreviations for names of rock-forming minerals. *Am. Mineral.* **2010**, *95*, 185–187. [[CrossRef](#)]
49. Kushiro, I.; Aoki, K. Origin of some eclogite inclusions in kimberlite. *Am. Mineral.* **1968**, *53*, 1347–1367.
50. Aoki, K. Origin of phlogopite and potassic richterite bearing peridotite xenoliths from South Africa. *Contrib. Mineral. Petrol.* **1975**, *53*, 145–156. [[CrossRef](#)]

51. McDonough, W.F.; Sun, S.S. The composition of the Earth. *Chem. Geol.* **1995**, *120*, 223–253. [\[CrossRef\]](#)
52. Ionov, D.A.; O'Reilly, S.Y.; Ashchepkov, I.V. Feldspar-bearing lherzolite xenoliths in alkali basalts from Hamar-Daban, southern Baikal region, Russia. *Contrib. Mineral. Petrol.* **1995**, *122*, 174–190. [\[CrossRef\]](#)
53. Sokol, A.G.; Kruk, A.N.; Chebotarev, D.A.; Pal'yanov, Y.N.; Sobolev, N.V. Conditions of phlogopite formation upon interaction of carbonate melts with peridotite of the subcratonic lithosphere. *Doklady Earth Sci.* **2015**, *462*, 638–642. [\[CrossRef\]](#)
54. Sokol, A.G.; Kruk, A.N.; Palyanov, Y.N.; Sobolev, N.V. Stability of phlogopite in ultrapotassic kimberlite-like systems at 5.5–7.5 GPa. *Contrib. Mineral. Petrol.* **2017**, *172*, 21. [\[CrossRef\]](#)
55. Francis, D.M. The origin of amphibole in lherzolite xenoliths from Nunivak Island, Alaska. *J. Petrol.* **1976**, *17*, 357–378. [\[CrossRef\]](#)
56. Delaney, J.S.; Smith, J.V.; Carswell, D.A.; Dawson, J.B. Chemistry of micas from kimberlites and xenoliths. II. Primary-secondary textured micas from peridotite xenoliths. *Geochim. Cosmochim. Acta* **1980**, *44*, 857–872. [\[CrossRef\]](#)
57. Arai, S. K/Na variation in phlogopite and amphibole of upper mantle peridotites due to fractionation of the metasomatizing fluids. *J. Geol.* **1986**, *94*, 436–444. [\[CrossRef\]](#)
58. Yaxley, G.M.; Green, D.H.; Kamenetsky, V.S. Carbonatite metasomatism in the southeastern Australian lithosphere. *J. Petrol.* **1998**, *39*, 1917–1930. [\[CrossRef\]](#)
59. Pirard, C.; Hermann, J. Experimentally determined stability of alkali amphibole in metasomatised dunite at sub-arc pressures. *Contrib. Mineral. Petrol.* **2015**, *169*, 1. [\[CrossRef\]](#)
60. Safonov, O.G.; Butvina, V.G. Interaction of model peridotite with H₂O-KCl fluid: Experiment at 1.9 GPa and its implications for upper mantle metasomatism. *Petrology* **2013**, *21*, 599–615. [\[CrossRef\]](#)
61. Edgar, A.D.; Arima, M. Experimental studies on K-metasomatism of a model pyrolite mantle and their bearing on the genesis of ultrapotassic magmas. In Proceedings of the 27th International Geological Congress, Moscow, Russia, 4–14 August 1984; Volume 9, pp. 509–541.
62. Thibault, Y.; Edgar, A.D. Patent mantle-metasomatism: Inferences based on experimental studies. *Proc. Ind. Acad. Sci. Earth Planet. Sci.* **1990**, *99*, 21–37. [\[CrossRef\]](#)
63. Ulmer, P.; Sweeney, R.J. Generation and differentiation of group II kimberlites: Constraints from a high-pressure experimental study to 10 GPa. *Geochim. Cosmochim. Acta* **2002**, *66*, 2139–2153. [\[CrossRef\]](#)
64. Foley, S.F.; Yaxley, G.M.; Rosenthal, A.; Buhre, S.; Kiseeva, E.S.; Rapp, R.P.; Jacob, D.E. The composition of near-solidus melts of peridotite in the presence of CO₂ and H₂O between 40 and 60 kbar. *Lithos* **2009**, *112*, 274–283. [\[CrossRef\]](#)
65. Enggist, A.; Chu, L.; Luth, R.W. Phase relations of phlogopite with magnesite from 4 to 8 GPa. *Contrib. Mineral. Petrol.* **2012**, *163*, 467–481. [\[CrossRef\]](#)
66. Enggist, A.; Luth, R.W. Phase relations of phlogopite and pyroxene with magnesite from 4 to 8 GPa: KCMAS–H₂O and KCMAS–H₂O–CO₂. *Contrib. Mineral. Petrol.* **2016**, *171*, 88. [\[CrossRef\]](#)
67. Dawson, J.B.; Smith, J.V. The MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths in kimberlite. *Geochim. Cosmochim. Acta* **1977**, *41*, 309–323. [\[CrossRef\]](#)
68. Grégoire, M.; Bell, D.; Le Roex, A. Trace element geochemistry of phlogopite-rich mafic mantle xenoliths: Their classification and their relationship to phlogopite-bearing peridotites and kimberlites revisited. *Contrib. Mineral. Petrol.* **2002**, *142*, 603–625. [\[CrossRef\]](#)
69. Kushiro, I.; Erlank, A.J. Stability of potassic richterite. *Carnegie Inst. Wash. Yearb* **1970**, *68*, 231–233.
70. Sudo, A.; Tatsumi, Y. Phlogopite and K-amphibole in the upper mantle: Implication for magma genesis in subduction zones. *Geophys. Res. Lett.* **1990**, *17*, 29–32. [\[CrossRef\]](#)
71. Konzett, J.; Sweeney, R.J.; Thompson, A.B.; Ulmer, P. Potassium amphibole stability in the upper mantle: An experimental study in a peralkaline KNCMAH system to 8.5 GPa. *J. Petrol.* **1997**, *38*, 537–568. [\[CrossRef\]](#)
72. Konzett, J.; Ulmer, P. The stability of hydrous potassic phases in lherzolitic mantle—An experimental study to 9.5 GPa in simplified and natural bulk compositions. *J. Petrol.* **1999**, *40*, 629–652. [\[CrossRef\]](#)
73. Yagi, A.; Suzuki, T.; Akaogi, M. High pressure transitions in the system KAlSi₃O₈–NaAlSi₃O₈. *Phys. Chem. Minerals* **1994**, *21*, 12–17. [\[CrossRef\]](#)
74. Fasshauer, D.W.; Wunder, B.; Chatterjee, N.D.; Höhne, G.W. Heat capacity of wadeite-type K₂Si₄O₉ and the pressure-induced stable decomposition of K-feldspar. *Contrib. Mineral. Petrol.* **1998**, *131*, 210–218. [\[CrossRef\]](#)
75. Meyer, H.O.A.; McCallum, M.E. Mineral inclusions in diamonds from the Sloan kimberlites, Colorado. *J. Geol.* **1986**, *94*, 600–612. [\[CrossRef\]](#)

76. Bulanova, G.P.; Argunov, K.P. Inclusions of K-feldspar in diamond crystal from the “Mir” pipe. *Doklady Akad. Nauk SSSR Earth Sci.* **1985**, *284*, 953–956.
77. Otter, M.; Gurney, J.J. Mineral inclusions in diamonds from the Sloan diatremes, Colorado-Wyoming state line kimberlite district, North America. In *Kimberlites and Related Rocks. V.2 Their Crust/Mantle Setting: Diamonds and Diamond Exploration*; Blackwell: Jiangxi, China, 1989; pp. 1042–1053.
78. Novgorodov, P.G.; Bulanova, G.P.; Pavlova, L.A.; Mikhailov, V.N.; Ugarov, V.V.; Shebanin, A.P.; Argunov, K.P. Inclusions of potassic phases, coesite and omphacite in the coated diamond crystal from the “Mir” pipe. *Doklady Akad. Nauk SSSR Earth Sci.* **1990**, *310*, 439–443.
79. Davies, R.M.; Griffin, W.L.; O’Reilly, S.Y.; Doyle, B.J. Mineral inclusions and geochemical characteristics of microdiamonds from the DO27, A154, A21, A418, DO18, DD17 and Ranch Lake kimberlites at Lac de Gras, Slave Craton, Canada. *Lithos* **2004**, *77*, 39–55. [[CrossRef](#)]
80. Anand, M.; Taylor, L.A.; Misra, K.C.; Carlson, W.D.; Sobolev, N.V. Nature of diamonds in Yakutian eclogites: Views from eclogite tomography and mineral inclusions in diamonds. *Lithos* **2004**, *77*, 333–348. [[CrossRef](#)]
81. Shatsky, V.S.; Zedgenizov, D.A.; Ragozin, A.; Kalinina, V.V. Diamondiferous subcontinental lithospheric mantle of the northeastern Siberian Craton: Evidence from mineral inclusions in alluvial diamonds. *Gondwana Res.* **2015**, *28*, 106–120. [[CrossRef](#)]
82. Smyth, J.R.; Hatton, C.J. A coesite-sanidine grosspydite from the Roberts Victor kimberlite. *Earth Planet. Sci. Lett.* **1977**, *34*, 284–290. [[CrossRef](#)]
83. Wohletz, K.H.; Smyth, J.R. Origin of a Roberts Victor sanidine-coesite grosspydite: Thermodynamic considerations. In *Kimberlites II: The Mantle and Crust-Mantle Relationships*; Kornprobst, J., Ed.; Elsevier: Amsterdam, The Netherlands, 1984; pp. 33–42.
84. Schulze, D.J.; Helmstaedt, H. Coesite-sanidine eclogite from kimberlite: Products of mantle fractionation or subduction? *J. Geol.* **1988**, *96*, 435–443. [[CrossRef](#)]
85. Schmickler, B.; Jacob, D.E.; Foley, S.F. Eclogite xenoliths from the Kuruman kimberlites, South Africa: Geochemical fingerprinting of deep subduction and cumulate processes. *Lithos* **2004**, *75*, 173–207. [[CrossRef](#)]
86. Misra, K.C.; Anand, M.; Taylor, L.A.; Sobolev, N.V. Multi-stage metasomatism of diamondiferous eclogite xenoliths from the Udachnaya kimberlite pipe, Yakutia, Siberia. *Contrib. Mineral. Petrol.* **2004**, *146*, 696–714. [[CrossRef](#)]
87. Shatsky, V.S.; Ragozin, A.L.; Zedgenizov, D.A.; Mityukhin, S. Evidence for multistage evolution in a xenolith of diamond-bearing eclogite from the Udachnaya kimberlite pipe. *Lithos* **2008**, *105*, 289–300. [[CrossRef](#)]
88. Zedgenizov, D.A.; Ragozin, A.L.; Shatsky, V.S.; Griffin, W.L. Diamond formation during metasomatism of mantle eclogite by chloride-carbonate melt. *Contrib. Mineral. Petrol.* **2018**, *173*, 84. [[CrossRef](#)]
89. Wang, W. Formation of diamond with mineral inclusions of “mixed” eclogite and peridotite paragenesis. *Earth Planet. Sci. Lett.* **1998**, *160*, 831–843. [[CrossRef](#)]
90. Wendlandt, R.F.; Eggler, D.H. Stability of sanidine+forsterite and its bearing on the genesis of potassium magmas and the distribution of potassium in the upper mantle. *Earth Planet. Sci. Lett.* **1980**, *51*, 215–220. [[CrossRef](#)]
91. Ionov, D.A.; Gregoire, M.; Prikhod’ko, V.S. Feldspar–Ti-oxide metasomatism in off-cratonic continental and oceanic upper mantle. *Earth Planet. Sci. Lett.* **1999**, *165*, 37–44. [[CrossRef](#)]
92. Olafsson, M.; Eggler, D.H. Phase relations of amphibole, amphibole-carbonate and phlogopite-carbonate peridotite: Petrologic constraints on the asthenosphere. *Earth Planet. Sci. Lett.* **1983**, *64*, 305–315. [[CrossRef](#)]
93. Haggerty, S.E. Oxide mineralogy of the upper mantle. In *Oxide Minerals: Petrologic and Magnetic Significance*; Lindsley, D.H., Ed.; Reviews in Mineralogy; De Gruyter: Berlin, Germany, 1991; Volume 25, pp. 355–416.
94. Foley, S.; Höfer, H.; Brey, G. High-pressure synthesis of priderite and members of the lindsleyite-mathiasite and hawthorneite-yimengite series. *Contrib. Mineral. Petrol.* **1994**, *117*, 164–174. [[CrossRef](#)]
95. Konzett, J.; Yang, H.; Frost, D.J. Phase relations and stability of magnetoplumbite-and crichtonite-series phases under upper-mantle P–T conditions: An experimental study to 15 GPa with implications for LILE metasomatism in the lithospheric mantle. *J. Petrol.* **2005**, *46*, 749–781. [[CrossRef](#)]
96. Konzett, J.; Wirth, R.; Hauzenberger, C.; Whitehouse, M. Two episodes of fluid migration in the Kaapvaal Craton lithospheric mantle associated with Cretaceous kimberlite activity: Evidence from a harzburgite containing a unique assemblage of metasomatic zirconium-phases. *Lithos* **2013**, *182*, 165–184. [[CrossRef](#)]
97. Giuliani, A.; Kamenetsky, V.S.; Phillips, D.; Kendrick, M.A.; Wyatt, B.A.; Goemann, K. Nature of alkali-carbonate fluids in the sub-continental lithospheric mantle. *Geology* **2012**, *40*, 967–970. [[CrossRef](#)]

98. Butvina, V.G.; Vorobey, S.S.; Safonov, O.G.; Varlamov, D.A.; Bondarenko, G.V.; Shapovalov, Y.B. Experimental study of the formation of chromium-bearing priderite and yimengite as products of modal mantle metasomatism. *Doklady Earth Sci.* **2019**, *486*, 711–715. [[CrossRef](#)]
99. Almeida, V.; Janasi, V.; Svisero, D.; Nannini, F. Mathiasite-loveringite and priderite in mantle xenoliths from the Alto Paranaíba Igneous Province, Brazil: Genesis and constraints on mantle metasomatism. *Open Geosci.* **2014**, *6*, 614–632. [[CrossRef](#)]
100. Abersteiner, A.; Kamenetsky, V.S.; Goemann, K.; Golovin, A.V.; Sharygin, I.S.; Giuliani, A.; Rodemann, T.; Spetsius, Z.V.; Kamenetsky, M. Djerfisherite in kimberlites and their xenoliths: Implications for kimberlite melt evolution. *Contrib. Mineral. Petrol.* **2019**, *174*, 8. [[CrossRef](#)]
101. Sharygin, I.S.; Litasov, K.D.; Sharygin, V.V.; Shatskiy, A.F.; Ohtani, E. Genesis of djerfisherite in kimberlite-hosted mantle xenoliths. In Proceedings of the Goldschmidt Conference, Yokohama, Japan, 26 June–1 July 2016; p. 2812.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).