Article

Geochemistry of Magmatic and Xenocrystic Spinel in the No.30 Kimberlite Pipe (Liaoning Province, North China Craton): Constraints on Diamond Potential

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Received: 29 April 2019; Accepted: 23 June 2019; Published: 24 June 2019

Abstract: There are two genetic types of spinel (magmatic spinel crystallizing directly from kimberlite magma and xenocrystic spinel derived from mantle xenoliths) in the No.30 kimberlite pipe (Liaoning Province, North China Craton). Their geochemistry is investigated to reveal processes of diamond capture and resorption during kimberlite magmatism to constrain the diamond potential. Magmatic spinels are mostly euhedral to subhedral, 20 to 60 μm in size, and have compositional zones: the cores are classified as chromite with high Cr and Mg contents, and the rims are classified as magnetite with low Cr and high ferric Fe. The compositional trends suggest that magmatic spinel and olivine phenocrysts are crystallized contemporaneously during the early stages of kimberlite crystallization. During this period, temperature (T) and oxygen fugacity (fO2) values calculated at an assumed pressure of 1 GPa are in the range of 994–1274 ºC and 1.6–2.4 log fO2 units below the nickel-nickel oxide (NNO) buffer, respectively. The high values of fO2 suggest heavy diamond resorption during kimberlite magmatism. Estimated temperatures of xenocrystic spinel range from 828 to 1394 ºC, and their distributions indicate that only a small proportion of xenocrystic spinels are derived from the diamond stabilization field, which suggests a low potential of diamond capture. The low diamond capture and heavy diamond resorption during kimberlite magmatism contributed to the low diamond grade of the No.30 kimberlite.

Keywords: geochemistry; magmatic spinel; xenocrystic spinel; kimberlite; diamond potential

1. Introduction

Diamond exploration relies on mantle-derived “indicator minerals” because they commonly occur as inclusions within diamonds, and thus, play an important role in diamond formation. The widely utilized indicator minerals include garnet, chromite, clinopyroxene, and ilmenite [1–13]. The use of chromite in diamond exploration has concentrated on the recognition of grains similar in the major-element composition to chromite inclusions within diamonds [14]. Combined major and trace element compositions for chromite are used to distinguish the source rock of chromite and to discriminate mantle-derived xenocrysts from magmatic spinels [4]. In addition, the Zn-in-chromite thermometer (proposed by Ryan et al. [15] based on the strong temperature-dependence of the partitioning of Zn between chromite and olivine) further divides chromite xenocrysts from kimberlite into those derived from the diamond stability field and those from shallower, barren levels of
mantle [4,5]. Single-grain temperature estimates are projected onto known geotherm to obtain a depth of origin for each grain [16].

At present, the discrimination of mantle-derived materials (xenoliths and xenocrysts) entrained by kimberlite is the main tool to predict the grade and quality of diamonds transported by the kimberlite to the Earth’s surface. However, in recent years, more and more studies focusing on various morphological forms and surface features in natural diamond recovered from kimberlites, show that diamond resorption (dissolution) widely occur during kimberlite magma ascent, which greatly influences the grade and value of diamonds [17,18]. The diamond resorption is greatly controlled by the oxygen fugacity ($f_{O2}$) of the kimberlite magma [17,19–21]. A good understanding of the magmatic history of the kimberlite is necessary to ascertain whether diamonds could survive the rapid journey from the upper mantle to the surface of the Earth. It has been shown that spinel commonly forms throughout the kimberlite crystallization [22], and thus the morphology and composition of magmatic spinel may be useful in deciphering the kimberlite crystallization history [23,24], and the temperature and oxygen fugacity in kimberlite magma during magmatic spinel formation could be estimated [25].

In a previous study on xenocrystic spinels from the No.30 kimberlite (Liaoning Province, North China Craton), the authors suggested that the cores of the spinel (classified as magnesiochromite) were remnants of primary mantle xenocrysts, and the intermediate zones (classified as chromite) and the rims (classified as magnetite) formed during kimberlite magmatism [26]. In this study, we report the trace element concentrations of xenocrystic spinels and discuss the differences between magnesiochromites derived from the diamond stability field and those from the barren levels of the mantle [4]. The major element compositions of magmatic spinels are presented and compared with those of the rims in xenocrystic magnesiochromites. The temperature and oxygen fugacity of the No.30 kimberlite magma are estimated in order to discuss the diamond resorption. The diamond potential of the No.30 kimberlite is discussed on the basis of the trace elements signature and temperature estimates of the xenocrystic garnet xenocrysts [27] and spinel (this paper).

2. Samples and Methods

The samples in this study consist of 14 magmatic spinels and 51 xenocrystic spinels from the No.30 kimberlite pipe. The magmatic spinels were prepared as double-polished thin sections and their major compositions were analyzed in this study. Xenocrystic spinels were single crystals obtained by heavy mineral concentration and separation, and their morphology and major elements have been reported in a previous study by Zhu et al. [26]. In this study, we proceeded to analyze their trace element concentrations.

The major elements of magmatic spinel were analyzed at the State Key Laboratory for Mineral Deposit Research, Nanjing University, China, using a JAX 8100 Electron Probe Micro Analyzer (EPMA). The EPMA work was conducted by wavelength dispersive spectrometry (WDS). The analytical conditions were as follows: beam accelerating voltage 20 kV, beam current 20 nA, beam diameter 1 µm, and a counting time of 30 s. A number of natural, as well as synthetic standards, were used for calibration. For the operating conditions, the detection limit for major elements was 0.01 wt. %, and the accuracy was better than 1%. The proportion of Fe$^{2+}$ and Fe$^{3+}$ in the chrome spinel was calculated using stoichiometric and charge balance equations [28].

Trace elements in xenocrystic spinel were investigated at the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, using a Coherent GeoLasPro 193-nm Laser Ablation system coupled with an Agilent 7700× ICP-MS. For spot analysis, a 40 µm spot size was applied with an energy density of ~100 mJ per pulse and a repetition rate of 6 Hz. Each analysis contained 20 s for measuring the gas blank and 40 s for data acquisition. Different silicate glass reference materials, including BHVO-2G, BIR-1G, GSE-1G, and NIST610 were used as external standards and $^{57}$Fe as an internal standard to calibrate element contents. Quality control of time-dependent drift of sensitivity and mass discrimination was monitored by GSE-1G repeated after every eight analyses. The off-line data processing was performed using the ICPMSDataCal
program [29]. Values were cross-checked against standards BCR-2G. Analytical precision of ≤6% was indicated for most elements (Table S1 in Supplementary Materials).

3. Results

3.1. Morphology of Spinel

The No.30 kimberlite was heavily hydrothermally altered. However, the xenocrystic and magmatic spinels were very resistant to alteration and survived as primary minerals. The morphology of xenocrystic spinel has been described by Zhu et al. [26] and will not be repeated here. The magmatic spinels are pervasive in kimberlite, usually euhedral to subhedral, 20 to 60 µm in diameter, and strongly zoned from the chromite core to the magnetite rim (Figure 1A, Table 1). The chromite cores in some magmatic spinels are further divided into Ti-Al-Mg chromite core and Ti-Al chromite intermediate zone (Figure 1B, Table 1). Some spinels show small holes (Figure 1C) that may represent an incipient “lagoon” in an atoll-texture [23], which is the characteristic feature of magmatic spinel in Group I kimberlite [22,30].

Figure 1. Backscatter electron (BSE) images of magmatic spinels (A,B) and xenocrystic spinels (C,D) from the No.30 kimberlite. Magmatic spinels show compositional zones from the Ti-Al-Mg chromite core through the Ti-Al chromite intermediate to the magnetite rim, and spinel xenocrysts show compositional zones from xenocrystic magnesiochromite core through the Ti-Al-Mg chromite intermediate zone to the magnetite rim.

3.2. Chemical Composition of Spinel

Magmatic spinels and xenocrystic spinels show compositional zones (Figures 1 and 2). From the cores through the intermediate zones to the rims in the magmatic spinels, there is a continuous decrease in Cr$_2$O$_3$ (from 49.8–53.4 through 16.4–46.0 to 0.2–2.7 wt. %) and MgO contents (from 8.1–13.9 through 0.3–4.6 to 0.1–0.7 wt. %); the Al$_2$O$_3$ concentrations increase from the cores (4.6–6.5 wt. %) to the intermediate zones (4.5–8.5 wt. %) and decrease sharply in the rims (0.01–1.5 wt. %); the TiO$_2$ concentrations increase from the cores (3.5–4.6 wt. %) to the intermediate zones (5.2–10.3 wt. %) and decrease sharply in the rims (0.2–4.6 wt. %) (Figure 2, Table 1); and there is a continuous increase in Fe$_2$O$_3$ contents (from 7.2–9.7 through 10.2–13.1 to 57.8–65.9 wt. %). The cores of the xenocrystic spinels are discriminated by higher Cr$_2$O$_3$ and MgO and lower TiO$_2$ and Fe$_2$O$_3$ compared with magmatic spinels (Figure 2), which supports the xenocrystic origin [26]. The intermediate zones and rims of xenocrystic spinels are suggested to form in the host kimberlite magma and can be linked to the magmatic spinels [26]. As shown in Figure 2, the rims of xenocrystic spinels show
low Cr$_2$O$_3$, MgO, Al$_2$O$_3$, and high Fe$_2$O$_3$ contents, which can be linked to the rims in the magmatic spinels. The intermediate zones of xenocrystic spinels show a wider range in Al$_2$O$_3$ and Cr$_2$O$_3$ concentrations, which shows more affinity to the cores of the xenocrystic spinels rather than the cores of the magmatic spinels; however, their MgO, TiO$_2$, and Fe$_2$O$_3$ concentrations are consistent with the latter. Moreover, in the spinel prisms ([23] and references therein), the cores of the magmatic spinel and intermediate zones of xenocrystic spinels are classified as chromite, the rims of the magmatic spinels and xenocrystic spinels are classified as magnetite, and the cores of the xenocrystic spinels are classified as xenocrysts (Figure 3).

Figure 2. Variations of MgO (A), Al$_2$O$_3$ (B), TiO$_2$ (C), and Fe$_2$O$_3$ (D) versus Cr$_2$O$_3$ contents in the magmatic and xenocrystic spinels from the No.30 kimberlite.
Figure 2. Variations of MgO (A), Al₂O₃ (B), TiO₂ (C), and Fe₂O₃ (D) versus Cr₂O₃ contents in the magmatic and xenocrystic spinels from the No.30 kimberlite.

Figure 3. Three spinel projections of oxidized spinel prism for magmatic and xenocrystic spinels from the No.30 kimberlite pipe: (A) Cr/(Cr + Al) versus Fe²⁺/(Fe²⁺ + Mg), (B) Fe³⁺/(Fe³⁺ + Al + Cr) versus Fe²⁺/(Fe²⁺ + Mg) and (C) Fe³⁺-Al-Cr. The iso-potential lines (dotted lines) indicating that the composition of the spinels that is in equilibrium with olivine (Fo 90 and 80) at a constant temperature of 1200 °C and 1100 °C is after Irvine (1965). Curves of trend 1 and trend 2 are after Mitchell [22] and Roeder and Schulze [23]. Abbreviations: Xen = xenocryst peridotite spinel; MUM = magnesium-ulvöspinel-magnetite; Chr = chromite; Xen' = Metasomatized xenocryst peridotite spinel; Mag = magnetite.
Table 1. Mineral chemistry (oxide wt. %) of magmatic spinels from the No.30 kimberlite.

| Oxide (wt. %) | WFD148-SP1 | WFD148-SP2 | WFD148-SP3 | WFD148-SP4 | WFD148-SP5 | WFD148-SP6 | WFD148-SP7 |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| TiO₂         | 3.84        | 0.35        | 3.92        | 0.79        | 3.99        | 0.69        | 4.20        |
| Al₂O₃        | 6.49        | 0.03        | 5.76        | 0.22        | 5.30        | 0.34        | 4.65        |
| Cr₂O₃        | 51.86       | 1.57        | 51.67       | 0.72        | 50.11       | 0.53        | 50.04       |
| Fe₂O₃        | 7.47        | 65.47       | 7.38        | 63.38       | 92.2        | 63.36       | 82.3        |
| FeO          | 21.21       | 30.72       | 21.92       | 29.34       | 23.21       | 29.14       | 23.80       |
| MgO          | 9.85        | 0.17        | 9.18        | 0.51        | 8.18        | 0.56        | 7.63        |
| MnO          | 0.58        | 0.01        | 0.56        | 0.18        | 0.81        | 0.09        | 0.80        |
| Total        | 101.30      | 98.71       | 100.38      | 95.14       | 100.53      | 94.71       | 100.46      |
| Cr/ (Cr + Al)| 0.096       | 0.010       | 0.100       | 0.024       | 0.102       | 0.021       | 0.090       |
| Al/Fe₂O₃     | 0.255       | 0.002       | 0.230       | 0.011       | 0.213       | 0.016       | 0.259       |
| Cr            | 1.366       | 0.048       | 1.383       | 0.023       | 1.353       | 0.017       | 1.349       |
| Fe³⁺/Fe²⁺     | 0.870       | 1.930       | 1.880       | 1.919       | 1.995       | 1.925       | 1.969       |
| Mg            | 0.499       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
| Mg            | 0.489       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
| Mg            | 0.489       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
| Mg            | 0.489       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
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| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
| Cr            | 1.366       | 0.048       | 1.383       | 0.023       | 1.353       | 0.017       | 1.349       |
| Fe³⁺/Fe²⁺     | 0.870       | 1.930       | 1.880       | 1.919       | 1.995       | 1.925       | 1.969       |
| Mg            | 0.489       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
| Mg            | 0.489       | 0.010       | 0.463       | 0.030       | 0.416       | 0.034       | 0.388       |
| Mg/Fe³⁺      | 0.649       | 0.000       | 0.016       | 0.006       | 0.024       | 0.003       | 0.023       |
| Mg/Fe²⁺      | 1.591       | 1.000       | 0.620       | 0.987       | 0.665       | 0.984       | 0.679       |
The trace element concentrations in the xenocrystic spinels from the No.30 kimberlite are shown in Figure 4 and Table 2, with Zn (320–1047 ppm), Ga (6.4–102 ppm), Zr (0.1–11.3 ppm), Nb (0.1–7.1 ppm), and Ni (668–2306 ppm). Most element concentrations are too low to meet the detection limit, and thus, are not shown here.

Figure 4. Variations of Cr$_2$O$_3$ (A), Al$_2$O$_3$ (B), TiO$_2$ (C), Ni (D), Zr (E), and Nb (F) versus T$_{Zn}$ in the cores of the xenocrystic spinels from the No.30 kimberlite. The T$_{Zn}$ are the temperature estimates based on the Zn-in-chromite thermometer [15].
Table 2. Trace element concentrations and equilibrium temperature estimated using the Zn-in-chromite method [15] in the xenocrystic spinels from the No.30 kimberlite.

| ppm     | L30-01 | L30-02 | L30-03 | L30-04 | L30-05 | L30-06 | L30-07 | L30-08 | L30-09 | L30-10 | L30-11 | L30-12 | L30-13 | L30-14 | L30-15 | L30-16 | L30-17 |
|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Zn      | 1047   | 452    | 662    | 453    | 571    | 657    | 910    | 850    | 803    | 482    | 698    | 677    | 609    | 358    | 375    | 363    | 359    |
| Ga      | 85.6   | 22.7   | 20.1   | 40.9   | 17.3   | 12.1   | 52.5   | 25.9   | 75.1   | 27.9   | 37.8   | 46.5   | 24.5   | 27.4   | 26.5   | 27.0   | 39.2   |
| Zr      | 0.23   | 0.83   | 6.13   | 1.44   | 0.36   | 1.12   | 1.97   | 0.17   | 0.15   | 1.80   | 0.51   | 0.16   | 0.24   | 5.35   | 5.31   | 5.44   | 3.09   |
| Nb      | 2.74   | 1.22   | 2.43   | 2.06   | 1.37   | 0.30   | 1.87   | 0.07   | 0.62   | 1.59   | 0.12   | 0.38   | 1.00   | 2.39   | 2.26   | 2.18   | 2.07   |
| Ni      | 696    | 957    | 994    | 1147   | 788    | 843    | 731    | 668    | 1327   | 977    | 1490   | 1373   | 750    | 1432   | 1437   | 1425   | 1821   |
| T<sub>Zn</sub> (°C) | 828    | 1177   | 995    | 1176   | 1059   | 998    | 874    | 898    | 919    | 1143   | 973    | 986    | 1031   | 1316   | 1286   | 1307   | 1316   |
| ppm     | L30-18 | L30-19 | L30-20 | L30-21 | L30-22 | L30-23 | L30-24 | L30-25 | L30-26 | L30-27 | L30-28 | L30-29 | L30-30 | L30-31 | L30-32 | L30-33 | L30-34 |
| Zn      | 551    | 610    | 751    | 764    | 723    | 648    | 595    | 729    | 611    | 588    | 478    | 416    | 479    | 479    | 655    | 806    | 411    | 320    |
| Ga      | 15.4   | 41.5   | 62.7   | 29.1   | 101.5  | 61.0   | 38.1   | 13.8   | 10.1   | 51.4   | 17.2   | 20.8   | 26.3   | 35.5   | 38.3   | 65.9   | 88.0   |
| Zr      | 4.02   | 0.11   | 0.07   | 0.20   | 1.32   | 0.28   | 1.62   | 2.36   | 9.31   | 1.41   | 0.41   | 2.74   | 2.35   | 3.25   | 4.82   | 10.39  | 11296  |
| Nb      | 1.19   | 0.65   | 0.07   | 0.49   | 3.39   | 0.71   | 2.16   | 1.37   | 2.32   | 1.38   | 1.00   | 1.38   | 1.04   | 1.37   | 1.46   | 2.95   | 3.83   |
| Ni      | 957    | 1435   | 978    | 702    | 1494   | 832    | 927    | 778    | 858    | 1491   | 808    | 955    | 1024   | 1563   | 1361   | 2041   | 2306   |
| T<sub>Zn</sub> (°C) | 1077   | 1030   | 944    | 938    | 959    | 1004   | 1041   | 956    | 1029   | 1047   | 1147   | 1146   | 1146   | 1100   | 918    | 1231   | 1394   |
| ppm     | L30-35 | L30-36 | L30-37 | L30-38 | L30-39 | L30-40 | L30-41 | L30-42 | L30-43 | L30-44 | L30-45 | L30-46 | L30-47 | L30-48 | L30-49 | L30-50 | L30-51 |
| Zn      | 660    | 655    | 815    | 695    | 478    | 815    | 520    | 419    | 903    | 452    | 751    | 397    | 484    | 736    | 809    | 793    | 524    |
| Ga      | 6.4    | 7.4    | 53.3   | 79.0   | 47.9   | 29.0   | 46.0   | 29.7   | 15.1   | 49.6   | 13.1   | 18.6   | 85.5   | 17.0   | 87.8   | 23.3   | 39.3   |
| Zr      | 1.30   | 11.3   | 5.37   | 0.35   | 3.50   | 0.08   | 8.08   | 2.84   | 4.56   | 0.94   | 0.36   | 0.70   | 5.93   | 0.95   | 0.05   | 10.66  | 2.68   |
| Nb      | 0.35   | 3.21   | 5.05   | 3.99   | 1.80   | 0.81   | 1.36   | 2.38   | 1.64   | 0.63   | 3.25   | 3.33   | 1.15   | 0.10   | 2.13   | 7.07   | 1.82   |
| Ni      | 846    | 922    | 1059   | 1048   | 981    | 1317   | 931    | 1308   | 976    | 838    | 701    | 1451   | 858    | 1089   | 1064   | 1075   | 888    |
| T<sub>Zn</sub> (°C) | 996    | 999    | 913    | 975    | 1147   | 914    | 1105   | 1220   | 877    | 1177   | 944    | 1251   | 1141   | 952    | 916    | 924    | 1100   |
4. Discussion

4.1. Early Crystallization Sequence

An understanding of the texture and chemical composition of kimberlite minerals is difficult because of the lack of detailed experimental work on the crystallization history of kimberlite magma [22,31]. Commonly, the first minerals to crystallize from the kimberlite magma are olivine phenocrysts and chromite [22]. Within the No.30 kimberlite pipe, chromite in the magmatic spinel was found in the cores of zoned magmatic spinels. The zoning trend in magmatic spinels from the chromite core to the magnetite rim is typical for the kimberlite and magnetite rim and is considered to be a product of late-stage crystallization [22,23]. In addition, an atoll-texture shown in zoned spinel (Figure 1B) is typical in Group I kimberlite [22].

The spinel prism-diagram showing the variation in the composition of spinel is widely used to infer crystallization processes in kimberlite [22,23,32,33]. It uses either ferric iron (oxidized prism) or titanium (reduced prism) as the vertical axis. There are two typical compositional trends in kimberlite: trend 1 from chromite to magnesio-ulvospinel-magnetite and trend 2 of increasing titanium and ferric iron as a function of increasing Fe\(^{2+}/(Fe^{2+} + Mg)\) (Figure 3, [23]). Trend 1 is influenced by the high carbonate content of kimberlite melt which causes rapid crystallization of the minerals [23], and trend 2 is generally known to form by the co-crystallization of phlogopite that depletes melt in Mg and Al [22]. As shown in Figure 3, with the increasing of Fe\(^{2+}/(Fe^{2+} + Mg)\), Cr/(Cr + Al) decreases and Fe\(^{3+}/(Fe^{3+} + Al + Cr)\) increases from the cores to the rims in the magmatic spinels. This compositional trend in Figure 3 is similar to trend 2 but slightly deviates to the right of the outline suggested by Mitchell [22]. This indicates that besides the co-crystallization of phlogopite and spinel, another Mg-rich mineral, such as olivine, must be involved. This is consistent with the proposal by Roeder and Schulze [23] and Bussweiler et al. [34] where trend 2 was shown to be caused by co-crystallization of olivine and phlogopite in kimberlites. In the Al-Cr-Fe\(^{3+}\) diagram (Figure 3C), the intermediate zones in the magmatic spinel show the compositional variation to trend 1 but appears different in the other plots (Figure 3A,B). Here, we explained that because the crystallization of large phlogopite prevented new phlogopite nucleation in the vicinity, local Al contents in the kimberlite magma increase during the crystallization of minerals (Table 1), and thus data points in Figure 3C are shifted from Trend 2 to the Trend 1 [23]. In summary, we conclude that spinel, olivine, and phlogopite are crystallized contemporaneously at the beginning of kimberlite crystallization.

4.2. Temperature and Oxygen Fugacity

Co-crystallized spinel-olivine pairs can be used to estimate the temperature and oxygen fugacity (fO\(_2\)) of the magma at the time of crystallization. The oxygen fugacity of kimberlite is an important parameter that influences diamond resorption [17,35,36]. Magmatic chromite compositions in this study suggest crystallization together with olivine phenocrysts (see Section 4.1). However, virtually all the olivine phenocrysts in the No.30 kimberlite were altered, and thus, their composition could not be obtained. An alternative method is to use the composition of olivine inclusion within chromite [37] which shows an average Mg\(^#\) (=Mg/(Mg + Fe) × 100) of 90. In this study, equilibrium temperatures are estimated using the spinel-olivine Fe/Mg exchange thermometer of O’Neill and Wall [38], as simplified by Ballhaus et al. [25]. As shown in Table 3, the calculated temperatures range from 994 to 1274 °C assuming a pressure of 1 GPa. Pressure has a fairly small effect on temperature (1.5% decrease in temperature from 10 kbar to 1 bar). The oxygen barometer is based on the olivine-orthopyroxene-spinel equilibrium developed by Ballhaus et al. [25]. This barometer requires the presence of orthopyroxene, and for orthopyroxene-undersaturated rocks, the barometer gives maximum oxygen fugacity values [25]. Because the silica activity (\(\delta_{SiO2}\)) of kimberlites is well below that required to stabilize orthopyroxene [39–43], a correction has to be made to the calculated fO\(_2\) values. Silica activity in the kimberlite can be limited by the groundmass mineral assemblages at a given temperature (T) and pressure (P) [22,30]. In this study, the upper limit of silica activity is...
constrained by the presence of monticellite, which is below the diopside-monticellite (Di-Mont) buffer. Silica activity for the Di-Mont buffer was calculated using the thermodynamic data of Holland and Powell [44], and the method of $f_{O_2}$ adjustment in this study was described in detail by Fedortchouk and Canil [35]. As shown in Table 3, the adjusted $f_{O_2}$ of the No.30 kimberlite ranges from 1.6 to 2.4 log units below the nickel-nickel oxide (NNO) buffer.

### Table 3. Equilibrium temperatures and oxygen fugacities estimated for the No.30 kimberlite magma by Ol-Sp thermobarometry assuming a pressure of 1 GPa.

| Sample       | Ol-Sp T (°C) | Ol-Sp Oxygen Fugacity | $\log f_{O_2}$ | $\log f_{O_2}^{FMQ}$ | $\log f_{O_2}^{NNO}$ | Corrected $f_{O_2}$ |
|--------------|--------------|-----------------------|-----------------|----------------------|----------------------|---------------------|
| WFD148-SP1   | 1249         | 1.5                   | −9.8            | 1.0                  | −1.40                | −0.41               | −1.5                | −2.0                |
| WFD148-SP2   | 1218         | 1.5                   | −10.1           | 1.1                  | −1.46                | −0.43               | −1.6                | −2.0                |
| WFD148-SP3   | 1168         | 1.9                   | −10.5           | 1.5                  | −1.54                | −0.46               | −1.4                | −1.8                |
| WFD148-SP4   | 1102         | 1.7                   | −11.7           | 1.3                  | −1.65                | −0.50               | −1.7                | −2.1                |
| WFD148-SP5   | 1181         | 2.0                   | −10.1           | 1.6                  | −1.52                | −0.45               | −1.1                | −1.6                |
| WFD148-SP6   | 1214         | 1.8                   | −10.0           | 1.4                  | −1.46                | −0.43               | −1.3                | −1.7                |
| WFD148-SP7   | 1265         | 1.6                   | −9.4            | 1.2                  | −1.38                | −0.40               | −1.3                | −1.7                |
| WFD165-SP8   | 1170         | 1.2                   | −6.9            | 0.8                  | −1.54                | −0.46               | −2.0                | −2.4                |
| WFD165-SP9   | 1274         | 1.5                   | −5.5            | 1.1                  | −1.36                | −0.40               | −1.4                | −1.8                |
| WFD165-SP10  | 1107         | 1.6                   | −7.3            | 1.2                  | −1.65                | −0.50               | −1.8                | −2.2                |
| WFD165-SP11  | 994          | 1.9                   | −8.6            | 1.5                  | −1.84                | −0.57               | −1.9                | −2.4                |
| WFD165-SP12  | 1233         | 1.6                   | −5.9            | 1.2                  | −1.43                | −0.42               | −1.5                | −1.9                |
| WFD165-SP13  | 1240         | 1.5                   | −5.9            | 1.1                  | −1.42                | −0.42               | −1.5                | −1.9                |
| WFD165-SP14  | 1217         | 1.3                   | −6.3            | 1.0                  | −1.46                | −0.43               | −1.7                | −2.1                |

| a Temperatures calculated from the Fe/Mg exchange Ol-Sp thermometer of O’Neill and Wall [38] and Ballhaus et al. [25]; b Oxygen fugacities at 1 GPa calculated for the fayalite-magnetite-quartz (FMQ) buffer from the oxygen barometer by Ballhaus et al. [25]; c Silica activity of Diopside-Monticellite (Di-Mont) and Enstatite-Forsterite (En-Fo) buffers calculated using thermodynamic data of Holland and Powell [44]. d Corrected values of oxygen fugacities of kimberlite calculated for silica activity of Diopside-Monticellite buffer [35]. The equation for nickel-nickel oxide (NNO) buffer is from Ballhaus et al. [25].

**4.3. Trace Element Concentration in the Diamond Window**

In diamond exploration, it is important to discriminate the indicator mineral that is derived from diamond stability field and that from the diamond-barren or no-diamond field. The composition characteristics of minerals in the diamond stability field are based on mineral inclusions in the diamond [14]. However, the relative scarcity of mineral inclusions in the diamond limits a comprehensive understanding of these characteristics. Griffin and Ryan [4] describe the diamond stability field as the “diamond window,” which can be defined as the range of $T_Ni$ (Ni-in-garnet thermometer) between the intersection of geotherm with the diamond-graphite equilibrium curve and the base of the lithosphere (unmodified lithosphere). According to the estimate by Griffin and Ryan’s for the Liaoning Province, there is a diamond window with temperatures between 900–1250 °C [4]. In this study, we use the major and trace element composition in xenocrystic spinels to redefine a slightly narrower temperature range (950–1200 °C) for the diamond window. In contrast to the approach by Griffin and Ryan, we use a multi-element approach to constrain the temperature range.

As shown in Figure 4, the distribution of major and trace element concentrations show an abrupt change when $T_{zn}$ (Zn-in-chromite temperature, [15]) moves through 950 and 1200 °C. The compositions in the xenocrystic spinel with temperature 950–1200 °C are nearly constant: Cr$_2$O$_3$ (60–66 wt. %), Al$_2$O$_3$ (0–8 wt. %), TiO$_2$ (0–1 wt. %), Ni (500–1000 ppm), Zr (0–3 ppm), and Nb (0–2 ppm), and are consistent with that of chromite inclusions in diamonds [14]. The Ni, Zr, and Nb concentrations in spinels with temperatures between 950–1200 °C are lower than those with temperatures higher than 1200 °C (Figure 4), which may indicate that higher-T spinels have interacted with asthenosphere-derived melts [4,45–47]. For the spinels with temperatures below 950 °C, the spinels show the hybrid features: inner feature of spinels in the graphite field (low Cr$_2$O$_3$ and high Al$_2$O$_3$ contents) and low-T modification (increasing Zr and Nb concentrations). Due to the paucity of studies on chromite metasomatism, it is difficult to distinguish between metasomatism and original trace element signatures. Because some low-T metasomatism, especially carbonatite or...
COH metasomatism can be related to diamond formation [11–13, 48–50], the lower T boundary of the diamond window is unclear, and further studies are needed to constrain this more precisely.

4.4. Diamond Potential in Kimberlite

Diamond formation in the mantle is generally considered to be a metasomatic process [51, 52]. The metasomatic agents react with the mantle rocks in which they infiltrate, and the diamond crystallizes as a consequence of different redox reactions. The oxidation state is likely controlled by $\text{Fe}^0$-$\text{Fe}^{2+}$-$\text{Fe}^{3+}$ components in oxide minerals like chromite [12]. Malkovets et al. [16] suggested that garnet and chromite play an important role in the diamond formation. Therefore, garnet and chromite are important indicators of minerals. In general, diamondiferous kimberlites sample both garnet and chromite, but low-grade pipes tend to sample only chromite [16]. As discussed in Section 4.3, the diamond window beneath the Liaoning Province is redefined. If kimberlite captures garnet and chromite from this field at the same time, it has great potential to capture diamonds without considering other factors.

The equilibrium temperatures in the garnet xenocrysts from the No.30 kimberlite pipe calculated using single grain Ni-in-garnet thermometer [53] ranges from 1100 to 1350 °C, with a peak at about 1150 °C (Figure 5; [27]). However, the calculated equilibrium temperatures of xenocrystic chromites from the No.30 kimberlite using single grain Zn-in-chromite [15] vary from 828 to 1394 °C, with a peak at about 950 °C (Figure 5, Table 2). The temperature distribution curves show that garnets and chromites are not distributed in the same way, which is similar to the low-grade Zarnitsa and Solokha kimberlites, and different from the high-grade Udachnaya and Lomonosova kimberlites [16]. It indicates that garnets have not overgrown with chromites and diamonds haven’t widely formed in mantle rock samples by the kimberlite (Figure 5) [16]. Thus even though the No.30 kimberlite sampled the garnet/chromite-bearing mantle rock from the diamond stability field, the diamond grade in the kimberlite is low because the sampled mantle rocks are diamond-barren [16] and the diamond window is narrow.

As previously suggested by Zhu et al. [26], the oxidizing environment also contributes to low-grade diamonds in the No.30 kimberlite. The estimated $fO_2$ of the No.30 kimberlite magma is 1.6–2.4 log units relative to NNO buffer during the early magmatism (Table 3). Ideally, the $fO_2$ in the No.30 kimberlite is compared with that of other kimberlites with different diamond grades in the North China Craton.
However, there is no such study on $fO_2$ or related studies. So in this study, we compare $fO_2$ of the No.30 kimberlite magma with $fO_2$ estimates for the Lac de Gras kimberlites (Slave craton, Canada) with different diamond grades [17]. As shown in Figure 6, the comparison shows that the $fO_2$ of the No.30 kimberlite magma is most similar to the $fO_2$ of the low-grade Ranch Lake kimberlite and significantly higher than the $fO_2$ of high-grade Misery and Beartooth kimberlites in the Lac de Gras area. As suggested by many researchers, high $fO_2$ promotes diamond resorption [17,20,21]. We conclude that diamond resorption in the No.30 kimberlite was strong, which contributed to the generally low diamond grade.

![Figure 6](http://www.mdpi.com/2075-163X/9/6/382/s1)

**Figure 6.** Estimated log $fO_2$ oxygen fugacity conditions ($\Delta$NNO; derived from Ol–Sp thermobarometry at an assumed pressure of 1 GPa) for the No.30 kimberlite (this study) compared with Misery, Beartooth, Panda, Grizzly, Leslie, and Ranch Lake kimberlites from the Lac de Gras area [17] (the numbers in parentheses represent diamond grades of kimberlites in units of carats/ton).

5. Conclusions

Magmatic spinels in the No.30 kimberlite pipe are euhedral to subhedral, 20–60 µm in diameter. These spinels are zoned from Ti-Al-Mg chromite through Ti-Al chromite to magnetite, suggesting co-crystallization of spinel and olivine phenocrysts during early kimberlite crystallization.

At an assumed pressure of 1 GPa, temperatures and oxygen fugacity of kimberlite magma are estimated in a range of 994–1274 °C and 1.6–2.4 log units below the NNO buffer, respectively, suggesting strong diamond resorption during kimberlite magmatism.

Temperature distribution curves of xenocrystic garnet and chromite show that the sampling of garnet does not overlap with that of chromite, which suggests the mantle rock sampled by the kimberlite is diamond-barren.

Low-diamond capture and heavy-diamond resorption during kimberlite magmatism lead to low-diamond grade in the No.30 kimberlite.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/9/6/382/s1, Table S1: Trace elements chemistry for standard.

**Author Contributions:** R.-Z.Z., P.N., G.-G.W., and J.-Y.D. did the field work; R.-Z.Z. analyzed the samples and interpreted the results; R.-Z.Z. and P.N. wrote the paper; R.-Z.Z., P.N., G.-G.W. and J.-Y.D. revised the manuscript. All authors read and approved the manuscript.

**Funding:** This research was funded by the Ministry of Land and Resources of the PRC (Grant No. 201404025) and China Scholarship Council (No. 201706190172).

**Acknowledgments:** We thank N.K., S.-N.L., T.B., A.-D.Z., B.H., and L.-L.C. for their help during field work. We would like to thank W.-L.Z. for their technical guide during the analysis of the major elements of spinel. We appreciate L.L. and J.-F.G. for their help during the analysis of the trace elements of the spinel. Thanks to the State Key Laboratory for Mineral Deposit Research, Nanjing University for their assistance in the experiment. We appreciate the constructive comments from the Academic Editor and two anonymous reviewers.
Conflicts of Interest: The authors declare no conflict of interest.

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