Magnetic Cr-Rich Spinel in Serpentinized Ultramasfic Complexes

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Abstract In comparison to the six spinel end-members in the spinel prism, magnetic information on the intermediate spinel compositions is relatively poorly established. To investigate magnetic properties of intermediate compositions of Cr-rich spinel, we collected 12 samples that might contain potentially magnetic Cr-rich spinel. On the basis of chemical composition analysis and physical magnetic behavior, magnetic Group A Fe-rich spinel (i.e., magnetite), magnetic Group B Cr-rich spinel, and paramagnetic Group C Cr-Al-rich spinel were identified. Magnetite is solely responsible for the natural remanent magnetization (NRM) in severely serpentinized samples from intraoceanic island arcs, orogenic exposures of ultramasfics, and back-arc continental lithosphere settings. Magnetic Group B Cr-rich spinel shows maximum unblocking temperatures of 200–280°C. Such temperatures permit Cr-rich spinel to contribute to magnetic anomalies up to about 8–12 km in terrestrial lithosphere settings, given a normal geothermal gradient of 25 K/km. The existence of magnetic Cr-rich spinel requires certain compositional conditions including a cation ratio of [Cr]/[Fe²⁺ + Fe³⁺] from 1.33 to 1.56 as well as a low oxide ratio of (Al₂O₃ + MgO)/ (Cr₂O₃ + FeO + Fe₂O₃) less than 10%. It is evident that compositions of spinels are related with the degree of serpentinization as Group A spinel is observed along the fractures between/among olivine grains in heavily serpentinized rocks. Spinels in Groups B and C seem to experience less severe metasomatic or hydrothermal alteration during serpentinization. Distribution of magnetic Cr-rich spinel along the fractures of silicates (mostly olivine) may support a chemical origin of the NRM. Thus, Cr-rich spinel is a potential NRM carrier and a source of magnetic anomalies in ultramasfic complexes.

1. Introduction

Spinel is commonly found as accessory minerals in terrestrial igneous rocks. In igneous and metamorphic petrology, spinels have been used as petrographic or provenance indicators (e.g., O’Brien et al., 2017). Among the eight phases of spinels, Cr-rich spinel drew special attention because it is the first phase to crystallize in mafic-ultramafic magmas, thus providing a pivotal clue for the evolution of planetary lithosphere (e.g., Barnes & Roeder, 2001; Bowles et al., 2009; Brachfeld & Hammer, 2006). In nature, Cr-rich spinels were documented in many terrestrial igneous rocks including submarine gabbros (e.g., Etiope et al., 2018), chromite ores (e.g., Kumar & Bhalla, 1984a, 1984b), kimberlites (e.g., Giuliani et al., 2017; Schulze, 2001), subaerially extruded olivine basalts (e.g., Bannister et al., 1998; Haggerty, 1976), island-arc volcanic rocks (e.g., Kamenskaya et al., 2015; Scheel et al., 2009), ultramasfic rocks (e.g., ter Maat et al., 2019), and Precambrian layered intrusions (e.g., Latypov et al., 2018). Presence of Cr-rich spinel has also been reported in lunar rocks (e.g., Hopkins et al., 2019; Wasilewski et al., 1977), Martian meteorites (e.g., Shearer et al., 2019; Weiss et al., 2000, 2002, 2008; Yu & Gee, 2005), angrites (McKibbin & O’Neill, 2018), and chondrites (Gattacceca et al., 2011; Kaeter et al., 2018; Kohout et al., 2007; Schmitz et al., 2016).

In metamorphic petrology, Cr-rich spinel is commonly observed in serpentinized peridotites (e.g., Sobolev & Logvinova, 2005; Stewart et al., 2016). As the most resistant phase to alteration from the primary magmatic source, Cr-rich spinel is a useful constituent in understanding the subduction-induced metamorphism of ultramasfic complexes (e.g., Kruckenber et al., 2013; Scott et al., 2019; Titus et al., 2002, 2007; Toy et al., 2010; Zadeh et al., 2017). Hence, the physicochemical analysis of Cr-rich spinel bears implications on the degree of low temperature metamorphism (i.e., serpentinization) in a subduction regime.

Minerals in the spinel group possess 32 oxygen anions and 24 cations in a single unit cell. In general, eight cations form a fourfold tetrahedral configuration and 16 cations constitute a sixfold octahedral...
configuration. Depending on the distribution of cations, two different spinel structures exist. A normal spinel has eight divalent cations in tetrahedral sites and 16 trivalent cations in octahedral sites. On the other hand, an inverse spinel has eight trivalent cations in tetrahedral sites and 16 mixed cations (8 divalent + 8 trivalent) in octahedral sites. Spinels compositions are usually plotted in the spinel prism (Stevens, 1944) because pure end-members are rare in nature. In the spinel prism, six end-members are chromite (FeCr2O4, normal), hercynite (FeAl2O4, normal), magnesiocromite (MgCr2O4, normal), magnesioferrite (MgFe2O4, inverse), magnetite (Fe3O4, inverse), and spinel (MgAl2O4, normal). For a Ti-rich spinel, magnetite and ulvöspinel (Fe2TiO4, inverse) form a solid solution with the exchange reaction of 2Fe3+ = Fe2+ + Ti4+. Broadly speaking, olivine also has a spinel structure (Fe2SiO4, normal; Mg2SiO4, normal).

Despite their common existence in igneous or metamorphic rocks, magnetic properties of spinels are often biased toward magnetite only. Of the six spinel end-members, only Fe3O4 and MgFe2O4 are magnetic at room temperature with spontaneous magnetizations of 480 kA/m (Akimoto, 1962) and 112 kA/m (O’Neill et al., 1992), respectively. Because four other spinel end members are paramagnetic at room temperature, magnetic properties of intermediate compositions often require a linear mixing model between/among spinel end-members. In natural rocks, Cr-rich spinels have seldom been reported as a carrier of natural remanent magnetization (NRM) with unblocking temperatures well above the room temperature (e.g., Clark et al., 1992; Hounslove, 1996; Kędzjałko-Hofmokel et al., 2008; Kumar & Bhalja, 1984a; Murthy & Krishnamacharyulu, 1994; Xu et al., 1997; Yu et al., 2001). Cr-rich spinel has also been reported as an NRM carrier in some sediments (e.g., Freeman, 1986; Jenness, 1959; Leslie et al., 1990). The main goal of this study is to demonstrate that intermediate compositions of Cr-rich spinels collected from serpentinitized ultramafic complex are capable of carrying a stable remanent magnetization.

2. Samples and Analysis

Samples from CY and TW contain two block samples (CY1, CY2, TW1, and TW2) (Figure 1 and Table 1). Sample CR was obtained from a chromite-rich layer in the Stillwater Complex, MN, USA (Selkin et al., 2009) (Figure 1 and Table 1). All other samples were taken to study crystallographic and magnetic fabrics by the Structural Geology Group at University of Wisconsin-Madison (e.g., Kruckenberg et al., 2013; Tikoff et al., 2010; Titus et al., 2002, 2007; Toy et al., 2010). A brief summary is provided of the sample locations (Table 1).

Three chips, ~1 cm in diameter and ~1 cm in height, were cut from each block sample. One specimen per block sample was alternating-field (AF) demagnetized using a Molspin AF demagnetizer. The other specimen was used for thermal demagnetization, in 40°C steps from 80°C to 600°C using a Magnetic Measurements MMTD80 thermal demagnetizer. In addition to NRM, NRM* is also considered (Table 2). NRM* is calculated by projecting the cumulative vector-difference curves toward the direction of initial NRM (Table 2).

To identify the magnetic phases, microscopic experiments were carried out on the third specimen using scanning electron microscopy (SEM) and electron microprobe. For microscopic analysis, we used a field emission scanning electron microscope JSM7000F and Cameca SX100 electron probe X-ray micro analyzer.

For quantitative analysis, 2 min peak countings and 1 min background countings were obtained in an accelerating voltage of 15–20 kV, 10 nA beam current, and 1 µm spot size. Metals are represented as bright contrast in all the images used in the present article because back-scattered SEM photography is used. Compositional data were determined by stoichiometric calculations using the equations of Barnes and Roeder (2001). Major element compositions of chromium spinels determined by the electron microprobe analysis are presented for AL-B, CR-C, CY-A, CY-B, LE1-C, LE9-C, MA-B, MA-C, MO-A, PE-A, PE-C, PY-A, RA-C1, RA-C2, TR-A, TW-B, and TW-C (Table 3). Sum of cations is set to be 24, as numbers of cations are calculated on the basis of 32 oxygens for a spinel system (Table 3).

3. Results

Demagnetization results are displayed in terms of total intensity variation of magnetization with vector projections as insets (Figures 3–5) using the commonly used PuffinPlot software package (Lurcock & Wilson, 2012). On the basis of demagnetization characteristics, microscopic observations, and major
Figure 1. An altitude map showing the sites sampled in this study. Base map is produced using the GeoMapApp software (http://www.geomapapp.org) Version 3.6.10 (Ryan et al., 2009). AL = Almklovdalen subcontinental mantle lithosphere, Norway; CR = chromite layer, Stillwater Complex, MN, USA; CY = Cypress ultramafic complex, San Juan Islands, WA, USA; LE1 and LE9 = Leka ultramafic complex, Norway; MA = Madeline chromite, WA, USA; MO = Mohelno ultramafic complex, Czech Republic; PE = Kozakov ultramafic complex, Czech Republic; PY = Lherz ultramafic complex, Ariège Department, France; RA = Tiebaghi ultramafic complex, New Caledonia, French unique collectivity, Pacific Ocean; TR = Trinity ultramafic complex, CA, USA; TW = Twin Sister ultramafic complex, WA, USA.

Table 1
Sample Locations

| Label | Location | Number of opaque phases | Phase A (magnetite) | Phase B (magnetic Cr-rich spinel) | Phase C (paramagnetic Cr-Al-rich spinel) |
|-------|----------|-------------------------|---------------------|-----------------------------------|-----------------------------------------|
| AL    | Almklovdalen subcontinental mantle lithosphere, Norway | 1 | AL-B | | |
| CR    | Chromite layer, Stillwater Complex, MN, USA | 1 | | CR-C | |
| CY    | Cypress ultramafic complex, San Juan Islands, WA, USA | 2 | CY-A | CY-B | |
| LE1   | Leka ultramafic complex, Norway | 1 | | LE1-C | |
| LE9   | Leka ultramafic complex, Norway | 1 | | LE9-C | |
| MA    | Madeline chromite, WA, USA | 2 | MA-B | MA-C | |
| MO    | Mohelno ultramafic complex, Czech Republic | 1 | MO-A | | |
| PE    | Kozakov ultramafic complex, Czech Republic | 2 | PE-A | PE-C | |
| PY    | Lherz ultramafic complex, Ariège Department, France | 1 | PY-A | | |
| RA    | Tiebaghi ultramafic complex, New Caledonia, French unique collectivity, Pacific Ocean | 2 | | RA-C1, RA-C2 | |
| TR    | Trinity ultramafic complex, CA, USA | 1 | TR-A | | |
| TW    | Twin Sister Ultramafic Complex, WA, USA | 2 | TW-B | TW-C | |
In particular, Groups A and B are magnetic at room temperatures.

3.1. Samples With Group C Cr-Al-Rich Spinel

Results from CR, LE1, LE9, and RA are paramagnetic at room temperature. A measurable magnetic signal (>5 × 10⁻⁸ Am²) is not recorded at all during the course of AF or thermal treatment. Samples from the Leka ultramafic complex (Figure 2c) contain massive subangular Cr-rich spinel grains.

Fine-grained Cr-Al-rich spinels occur within the serpentinitized veinlet of the Tiebaghi ultramafic complex (Figure 2c). In RA (Tiebaghi ultramafic complex complex), fractured crystals of two different spinel phases (RA-C1 and RA-C2) are intergrown (Figure 2c). In particular, the chemical composition of RA-C1 is nearly identical to those of spinel phases in LE1 and LE9 (Table 3). Compared to RA-C1, RA-C2 is enriched in Al, Mg, and Fe³⁺ (Table 3). Overall, paramagnetic samples contain Group C Cr-Al-rich spinel (Table 3).

### Table 3

| Spinels | N   | Al  | Cr  | Fe³⁺  | Fe²⁺  | Mg  | Others | STUS | ST |
|---------|-----|-----|-----|-------|-------|-----|--------|------|----|
| Group A spinel (magnetite) |     |     |     |       |       |     |        |      |    |
| CY-A    | 10  | 0.17(0.11) | 0.00(0.00) | 15.77(0.11) | 7.83(0.10) | 0.13(0.10) | 0.10 | 110.2 | S3  |
| MO-A    | 10  | 0.16(0.07) | 0.00(0.00) | 15.75(0.08) | 7.71(0.07) | 0.23(0.08) | 0.14 | 109.6 | S9  |
| PE-A    | 10  | 0.14(0.05) | 0.01(0.01) | 15.64(0.11) | 7.75(0.07) | 0.16(0.04) | 0.30 | 109.2 | S10 |
| PY-A    | 10  | 0.13(0.08) | 0.00(0.00) | 15.76(0.08) | 7.78(0.09) | 0.15(0.08) | 0.17 | 109.9 | S12 |
| TR-A    | 10  | 0.19(0.11) | 0.00(0.00) | 15.67(0.13) | 7.74(0.09) | 0.18(0.09) | 0.23 | 109.3 | S15 |
| Group B spinel (magnetic Cr-rich spinel) |     |     |     |       |       |     |        |      |    |
| AL-B    | 7   | 0.87(0.34) | 12.24(0.63) | 2.02(1.02) | 6.76(1.02) | 1.52(0.67) | 0.59 | 74.3  | S1  |
| CY-B    | 7   | 0.80(0.16) | 12.16(0.38) | 2.89(0.32) | 6.25(0.62) | 1.69(0.62) | 0.21 | 76.3  | S4  |
| MA-B    | 7   | 0.98(0.23) | 12.68(0.58) | 1.93(0.61) | 6.18(0.49) | 1.88(0.46) | 0.35 | 72.8  | S7  |
| TW-B    | 7   | 1.15(0.29) | 12.59(0.41) | 2.05(0.46) | 6.52(0.55) | 1.44(0.52) | 0.24 | 74.6  | S16 |
| Group C spinel (paramagnetic Cr-rich spinel) |     |     |     |       |       |     |        |      |    |
| CR-C    | 14  | 4.97(0.85) | 10.42(0.76) | 0.57(0.24) | 3.10(0.47) | 4.80(0.48) | 0.14 | 46.8  | S2  |
| LE1-C   | 11  | 5.11(1.31) | 10.22(1.35) | 0.58(0.21) | 3.02(0.39) | 4.91(0.39) | 0.16 | 45.9  | S5  |
| LE9-C   | 9   | 4.20(0.78) | 10.98(0.82) | 0.67(0.44) | 3.12(0.34) | 4.84(0.30) | 0.19 | 49.1  | S6  |
| MA-C    | 15  | 4.35(0.78) | 10.32(0.53) | 1.15(0.74) | 4.00(0.75) | 3.95(0.67) | 0.22 | 53.1  | S8  |
| PE-C    | 13  | 4.17(0.48) | 9.56(0.57) | 1.27(0.65) | 3.93(0.50) | 4.43(0.50) | 0.64 | 51.1  | S11 |
| RA-C1   | 11  | 4.33(0.80) | 10.62(1.03) | 0.89(0.99) | 3.67(0.59) | 4.28(0.58) | 0.21 | 38.6  | S13 |
| RA-C2   | 10  | 6.21(0.54) | 6.38(0.60) | 3.34(0.23) | 0.61(0.42) | 7.33(0.43) | 0.13 | 51.3  | S14 |
| TW-C    | 15  | 4.95(0.89) | 7.98(1.00) | 2.87(0.58) | 2.50(0.59) | 5.54(0.58) | 0.16 | 48.3  | S17 |

Note: N is the total number of electron microprobe analyses per sample. Values within brackets represent 1 standard deviation. STUS is the sum of total unpaired spins in a single unit cell of spinel. ST represents the supporting information tables.
3.2. Samples With Group A Fe-Rich Spinel (Magnetite)

Results from MO, PE, PY, and TR show the highest unblocking temperature of 580°C, hallmark for the presence of magnetite (Figure 3a). In other words, these samples contain Group A Fe-rich spinel (i.e., magnetite). NRM of Group A spinel ranges from $3.21 \times 10^{-6}$ to $6.04 \times 10^{-6}$ Am² (Table 2). Under the SEM, cubic magnetites (Fe₃O₄) are abundant with little contribution from other elements (Figure 3b and Table 3). Magnetite occurs along the boundary between olivine crystals and serpentine zones (Figure 3b). Concentration of fine-grained magnetite between olivine crystals and serpentine zones is common in all samples of MO, PE, PY, and TR. Olivine is progressively replaced with serpentine during serpentinization (e.g., Carbonin et al., 2015; Nadoll et al., 2014). If so, hydrothermal fluids associated with serpentinization are responsible for the concentration of fine-grained magnetite (e.g., Berndt et al., 2014; Evans, 2011; Maffione et al., 2014).

Magnetite is the only opaque phase in MO, PY, and TR, while two opaque phases occur in PE (PE-A and PE-C). In PE, it is apparent that PE-C is paramagnetic Group C Cr-Al-rich spinel (Table 3) as there is a single magnetic phase.

3.3. Samples With Group B Cr-Rich Spinel

After eradicating an initial viscous component at room temperature to ~80°C, thermal demagnetizations of AL, MA, TW-1, and TW-2 show a rapid decay of NRM at intermediate temperatures (80–200°C for MA; 80–280°C for AL, TW1, and TW2) (Figures 4a–4d). In these samples, presence of magnetic Group B spinel is responsible for the rapid decay of NRM at intermediate temperatures. NRM of Group B spinel varies from $2.07 \times 10^{-7}$ to $1.39 \times 10^{-6}$ Am² (Table 2).

In TW1, opaque phases are developed within the serpentine veinlets along the fractures of the olivine nodules (Figure 4e). While AL contains a single opaque phase of Group B Cr-rich spinel, MA and TW contain two opaque phases (Table 1). For example, intergrown subparallel spinel phases occur in TW1 (TW1-B and TW1-C) (Figure 4f). The highlighted rectangular area in Figure 4e is magnified in Figure 4f. MA contains dual opaque phases of Group B Cr-rich spinel and Group C Cr-Al-rich spinel, respectively. Then, it is evident that MA and TW contain both magnetic Group B spinel and paramagnetic Group C spinel (Table 3).

3.4. Samples With Group B Cr-Rich Spinel and Group A Fe-Rich Spinel (Magnetite)

Sample CY (Cypress Island, part of the Fidalgo ophiolite) is unique because it shows a mixed behavior. Both AF and thermal demagnetizations show a weak viscous component and two stable NRM components (Figures 5a–5d). It is apparent that two stable magnetization components show a maximum unblocking at ~240–280°C and ~580°C, respectively (Figures 5c and 5d). NRM of CY varies from $3.72 \times 10^{-6}$ to $2.05 \times 10^{-4}$ Am² (Table 2).

Opaque phases occur mainly along the fractures or often within the edge of the fractured olivine (Figure 5e). In a magnified scale, two spinel phases (CY1-A and CY1-B) seem to be present (Figure 5f). On the basis of electron microprobe analysis (Table 3), CY-A is identified as magnetic Group A spinel (i.e., magnetite). On the other hand, CY-B is a magnetic Group B spinel whose composition is fairly similar to those of AL-B, MA-B, and TW-B (Table 3).
4. Discussion

4.1. Magnetic Cr-Rich Spinel

Among 12 analyzed samples, 4 samples (CR, LE1, LE9, and RA) are paramagnetic, while 8 others are magnetic (Figures 2–5 and Table 3). On the basis of compositional analysis, we found that seven samples (AL, CR, LE1, LE9, MO, PY, and TR) contain a single spinel phase, while five others (CY, MA, PE, RA, and TW) contain dual spinel phases. However, the existence of dual spinel phases does not necessarily indicate a complicated magnetic behavior. For example, RA is paramagnetic, while MA, PE, and TW show only a single NRM component in thermal treatment (Figures 3 and 4).

Among 17 spinel phases identified from 12 samples, which are magnetic? We identified Group A spinel (i.e., magnetite) from CY-A, MO-A, PE-A, PY-A, and TR-A (Table 3). They display maximum unblocking temperature of 580°C during thermal demagnetization. The difficult issue is to assess the magnetic properties of magnetic Group B Cr-rich spinel and paramagnetic Group C Cr-Al-rich spinel. Because CR is paramagnetic, CR-C must be paramagnetic Group C spinel. If two spinel phases are observed in SEM/probe, it is possible to determine which one is magnetic because either the entire sample is paramagnetic or magnetite can be easily differentiated from Cr-rich spinel. As PE shows a single magnetic phase of magnetite during thermal demagnetization, we can safely exclude the PE-C as a paramagnetic Group C spinel.

On the basis of the following reasoning, we propose that Group B spinel is magnetic Cr-rich spinel, while Group C is paramagnetic Cr-Al-rich spinel. First, LE1-C, LE9-C, and RA (containing both RA-C1 and RA-C2) is paramagnetic (Table 1). In fact, LE1-C, LE9-C, and RA-C1 reveal nearly identical compositions (Table 3). Second, paramagnetic RA contains RA-C2, which also belongs to paramagnetic Group C spinel (Table 3). Third, AL-B is magnetic and shows a single spinel phase whose composition falls in magnetic Group B spinel (Table 3). Fourth, CY shows two magnetic components during thermal demagnetization and two spinel phases under the SEM (Figure 5). Compositions of two spinel phases of CY fall in magnetic Group A spinel (CY-A) and magnetic Group B Cr-rich spinel (CY-B), respectively (Table 3). Fifth, MA and TW contain two spinel phases, each of which falls in magnetic Group B Cr-rich spinel (MA-B, TW-B) and paramagnetic Group C Cr-Al-rich spinel (MA-C, TW-C). In summary, intermediate compositions of Group B Cr-rich spinel are magnetic at room temperatures.

4.2. Chemistry of Cr-Rich Spinel

Cation compositions of spinels are calculated with unit formulas based on 32 oxygens (Table 3). The cation sum of minor elements other than Cr, Al, Mg, Fe²⁺, and Fe³⁺ is insignificant, with mean values for each.
sample always limited to less than 0.64 out of 24 cations in a single spinel unit cell (Table 3). Compared to paramagnetic Cr-rich spinels, magnetic Cr-rich spinels are enriched in Cr, Fe$^{2+}$, and Fe$^{3+}$ but are depleted in Al and Mg (Table 3). Compositions of magnetite observed from CY-A, MO-A, PE-A, PY-A, and TR-A are similar to those of stoichiometric magnetites. For instance, the cation sum (23.60 for CY-A, 23.46 for MO-A, 23.39 for PE-A, 23.52 for PY-A, and 23.41 for TR-A) is close to 24, hence the maximum available impurity is less than 3% in these samples. In addition, the ratio of Fe$^{3+}$/Fe$^{2+}$ remains close to 2 (e.g., 2.01 for CY-A, 2.04 for MO-A, 2.02 for PE-A, 2.03 for PY-A, 2.02 for TR-A), suggestive of stoichiometric magnetite (Table 3).
To better constrain a possible correlation between the chemical composition and the magnetic behavior of the spinel phases, compositional data from electron microprobe analysis are plotted in ternary diagrams (Figure 6). A relatively high content of trivalent cations is most prominent in compositional analysis of spinels (Table 3). Thus, the results are displayed in ternary diagrams with three trivalent cations (Al$_2$O$_3$, Cr$_2$O$_3$, and Fe$_2$O$_3$) at the apexes (Figure 6a). Three distinct groups are identified as paramagnetic Cr-Al-rich spinels (Figure 6b). Paleomagnetic analysis was carried out using the PuffinPlot software (https://www.talvi.net/puffinplot/) Version 1.4.1 (Lurcock & Wilson, 2012). In vector projections, blue and black squares represent vertical and horizontal plane projections. (e) Under the SEM, opaque phases occur along the fractures or often within the edges of the fractured olivine. (f) In a magnified scale, two spinel phases seem to present as Group A spinel (CY1-A) and Group B Cr-rich spinel (CY1-B). Ol = olivine; Srp = serpentine; Cr-s = Cr-rich spinel; Mag = magnetite; CY1-A = Group A spinel (magnetite); CY1-B = Group B Cr-rich spinel.

Figure 5. (a, b) Alternating-field (AF) and (c, d) thermal demagnetization of CY shows a weak viscous component and two stable NRM components. Two stable magnetization components show a maximum unblocking at ~240–280°C and ~580°C, respectively. Paleomagnetic analysis was carried out using the PuffinPlot software (https://www.talvi.net/puffinplot/) Version 1.4.1 (Lurcock & Wilson, 2012). In vector projections, blue and black squares represent vertical and horizontal plane projections. (e) Under the SEM, opaque phases occur along the fractures or often within the edges of the fractured olivine. (f) In a magnified scale, two spinel phases seem to present as Group A spinel (CY1-A) and Group B Cr-rich spinel (CY1-B). Ol = olivine; Srp = serpentine; Cr-s = Cr-rich spinel; Mag = magnetite; CY1-A = Group A spinel (magnetite); CY1-B = Group B Cr-rich spinel.
Five samples (CY-A, MO-A, PE-A, PY-A, and TR-A) are magnetite ($\text{Fe}_3\text{O}_4$). Twelve other Cr-rich spinel phases form a rather scattered distribution (Figure 6a). As the distinction between metal cations with unpaired electrons and metal cations without unpaired electrons is likely to control the magnetic behavior of spinels, the ternary diagram is slightly modified to incorporate the total Fe content ($\text{FeO} + \text{Fe}_2\text{O}_3$) as well as the dominant metal cations without unpaired electrons ($\text{MgO} + \text{Al}_2\text{O}_3$) (Figure 6b). When the ($\text{FeO} + \text{Fe}_2\text{O}_3$) and ($\text{MgO} + \text{Al}_2\text{O}_3$) apexes are used, 12 Cr-rich spinels show tighter clustering (Figure 6b) than those without FeO and MgO (Figure 6a).

We compared the Cr# ($=\frac{\text{[Cr]}}{\text{[Cr} + \text{Al]}}$) and Mg# ($=\frac{\text{[Mg]}}{\text{[Mg} + \text{Fe}^{2+}]$}) of spinels with the references values determined from spinel-xenoliths of various origin (Figure 7). Primary spinel-xenoliths in ophiolite are commonly produced by crystal fractionation of lithospheric material or by metasomatic processes (Paktunc, 1990). The most distinct compositional difference between the xenoliths in ophiolite (Dick & Bullen, 1984) and those in kimberlites (Haggerty, 1979) is depletion of aluminum and enrichment of chromium (Figure 7a). Diamond inclusions (Daniels & Gurney, 1991) possess very high Cr#. About half of data in Group C fall neither in the ophiolitic zone nor on kimberlite zone of primary spinels (Figure 7a). Instead, observed data fit better with evolutionary trends of secondary spinels (Figure 7b). Most data in Group C fall within the metasomatic envelop (Haggerty, 1991), which are characterized with high Mg# (Figure 7b). The Group B spinels appear to define two distinctive trends, one toward very high Mg# associated with secondary spinels of metamorphic origin (Figure 7b). The other trend is directed to lower Mg#, suggesting a mixture of secondary spinels of metasomatic and metamorphic origin (Figure 7b). None of the results in this study overlap with secondary groundmass in kimberlite (Haggerty, 1979) or ophiolite and fracture zone fields (Kimball, 1990). In this study, chemical analysis points at the role of secondary hydrothermal alteration of spinels (e.g., Kimball, 1990). It is possible that chromium is preferentially retained in spinel, while aluminum is progressively migrated to form alteration phases during hydrothermal alteration (e.g., Haggerty, 1991).
Both compositional analysis and microscopic observations indicate that spinels in Groups B and C seem to experience metasomatic or hydrothermal alteration during serpentinization (Figure 7).

Compositional data of spinels in this study are obviously different from those collected in lunar missions (Figure 8). Such discordance can be explained by the fundamental difference of chemical composition for the lunar spinel whose composition is dictated by FeCr$_2$O$_4$–FeAl$_2$O$_4$–Fe$_2$TiO$_4$ solid solution series (e.g., Haggerty, 1972).

4.3. Intermediate Compositions of Cr‐Rich Spinel

Regardless of the origin of NRM, intermediate compositions of Group B Cr‐rich spinel can be magnetic, thus can contribute to NRM. Cr‐rich spinel can entirely constitute the NRM (Figure 4) or it can dominate the NRM while coexisting with magnetite (Figure 5). In particular, Cr‐rich spinel often records $T_c$ of 200–350°C both in terrestrial (e.g., Hounslow, 1996; Kędziołka‐Hofmokl et al., 2008; Kumar & Bhalla, 1984a; Murthy & Krishnamacharyulu, 1994; O’Driscoll & Petronis, 2009; Xu et al., 1997; Yu et al., 2001) and in extraterrestrial (e.g., Yu & Gee, 2005) materials. In this study, Group B spinel shows maximum unblocking temperatures of 200–280°C. Such temperatures permit Cr‐rich spinel to contribute to magnetic anomalies up to about 8–12 km, given a reasonable geothermal gradient of 25 K/km. Thus, Cr‐rich spinel should be considered as an NRM carrier and as potential source of magnetic anomalies in planetary lithospheres (e.g., Clark et al., 1992; Nazarova, 1994). Establishing the detailed rock magnetic information, as well as the chemical characterization, for the intermediate compositions of spinel solid‐solution series is needed to strengthen our understanding of the planetary lithosphere.

The spinel prism includes six end‐members of chromite (FeCr$_2$O$_4$), hercynite (FeAl$_2$O$_4$), magnesiochromite (MgCr$_2$O$_4$), magnesioferrite (MgFe$_2$O$_4$, inverse), magnetite (Fe$_3$O$_4$, inverse), and spinel (MgAl$_2$O$_4$, normal). For a Ti‐rich spinel, magnetite can be replaced with ulvöspinel (Fe$_2$TiO$_4$).
systems are used. To better understand the observed unblocking temperatures of the Group B spinel, five individual binary solid solution series deserves to be addressed. The first binary system is a magnetite-spinel solid solution series \( [(Fe_3O_4)_{1-x}(MgAl_2O_4)_x] \). The distribution of cations between the tetrahedral and octahedral sublattices for magnetite-spinel solid solution series is beyond the scope of the present study, but was provided elsewhere (e.g., Harrison & Putnis, 1998; Nell et al., 1989; Nell & Wood, 1989). According to Harrison and Putnis (1995, 1996, 1997), magnetic properties of binary magnetite-spinel solid solution are strongly composition dependent. The magnetite-spinel solid solution series is ferrimagnetic at room temperature for \( x > 0.3 \) with the octahedral sublattice magnetization greater than the tetrahedral sublattice magnetization (Harrison & Putnis, 1995). The inverse is true for \( x < 0.3 \) (Harrison & Putnis, 1995). The \( x = 0.3 \) composition is a compensation point associated with antiferromagnetism (Harrison & Putnis, 1995). Replacing \( Mg^{2+} \) for \( Fe^{2+} \) in tetrahedral sites has very little effect on the ordering behavior, implying that \( Mg^{2+} \) and \( Fe^{2+} \) shares similar site preference (Harrison & Putnis, 1995). For a normal spinel (e.g., \( MgAl_2O_4 \)), the normal ordering is anticipated with a strong tetrahedral site preference of \( Mg \) over \( Al \). On the contrary, the inverse ordering is expected with a strong tetrahedral site preference of \( Fe^{2+} \) over \( Fe^{3+} \) for an inverse spinel (e.g., \( Fe_3O_4 \)). Such preference leads to an increase of \( Al \) on tetrahedral sites as the temperature increases (Harrison & Putnis, 1998).

A second binary system is a titanomagnetite solid solution series \( [(Fe_3O_4)_{1-x}(Fe_2TiO_4)_x] \). Although our samples do not contain significant amount of \( Ti \), titanomagnetite solid solution deserves to be mentioned as it is the most well-established solid solution in the spinel prism. For different degrees of cation ordering, there is little variation in \( T_c \) for titanomagnetite solid solution series (e.g., Lattard et al., 2012; Moskowitz, 1987). On the contrary, variation in \( T_c \) is rather high for magnetite-spinel solid solution (Harrison & Putnis, 1996).

A third binary system is a magnetite-fayalite or magnetite-forsterite solid solution series. Magnetic behavior of spinelloid solid solution series in the system \( Fe_3O_4-Fe_2SiO_4 \) or \( Fe_3O_4-(Mg,Fe)_2SiO_4 \) was investigated as an explanation for the notably high magnetic anomalies reported for Mars (Konny et al., 2004). According to Kontny et al. (2004), \( T_c \) decreases with increasing \( Si \) content with a rate of 8.3–10.9 K per percent in the spinel structure.

A fourth binary system is an ulvöspinel-chromite solid solution series. \( FeCr_2O_4 \) with the cation distribution \( Fe^{2+}(Cr^{3+})_2O_4 \) has a ferrimagnetic Curie temperature \( T_c \approx 70 \) K. The magnetic moment of \( FeCr_2O_4 \) at 4.2 K is weak due to spin canting or spin reversal (e.g., Derbyshire & Yearian, 1958; Robbins et al., 1971). Oxidation involves cation deficiency, by removing \( Cr^{3+} \) preferentially. Strong interaction between tetrahedral and octahedral sublattice is responsible for the enhanced Curie point of cation deficient \( FeCr_2O_4 \) as high as 520 K (Schmidbauer, 1987).

A fifth binary system is a magnetite-chromite solid solution series \( Fe(Fe_1-xCr_x)_{2}O_4 \). Because \( Cr^{3+} \) cations have very high octahedral site preference, we can ignore tetrahedral \( Cr^{3+} \). Then, \( Fe^{2+} \) and \( Fe^{3+} \) cations can occupy both tetrahedral and octahedral sites (Kurepin, 2005). Spinel binaries formed by mixing two identical types of spinels (i.e., normal + normal or inverse + inverse) are nearly ideal, and their analysis is straightforward (Ziemiak & Castelli, 2003). However, the inverse–normal spinel mixtures may exhibit immiscibility. In the chromite-rich region \( 0 \leq x \leq 1/3 \), \( Fe^{2+} \) ions are present only on octahedral sites. Therefore, substituting \( Cr^{3+} \) for \( Fe^{2+} \) occurs only on octahedral sites for \( 0 \leq x \leq 1/3 \) (Ziemiak & Castelli, 2003). In the magnetite-rich region \( 2/3 \leq x \leq 1 \), substitution of \( Cr^{3+} \) cations removes equal amounts of \( Fe^{3+} \) and \( Fe^{2+} \) cations from octahedral sites, so that \( Fe^{2+} \) cations begin to appear on tetrahedral sites (Ziemiak & Castelli, 2003). For \( 2/3 \leq x \leq 1 \), octahedral \( Fe^{3+} \) and \( Fe^{2+} \) cations become nearly indistinguishable due to a rapid electron exchange reaction, known as the electron hopping phenomenon. There exists a transition zone \( 1/3 \leq x \leq 2/3 \) where a complicated cation disorder occurs.

We observed maximum unblocking of 200–280°C for samples containing the Group B spinel. It is true that the Group B spinel is far from being a simple binary mixture, yet it is still possible to crudely predict the \( T_c \) of intermediate compositions of spinel system. Values of \( T_c \) are available in the literature (Figure 9) for four sets of binary systems including magnetite-fayalite or magnetite-forsterite (Konny et al., 2004; Yamanaka & Okita, 2001), magnetite-spinel (Harrison & Putnis, 1996; Nishitani, 1981), magnetite-ulvöspinel (Lattard et al., 2006), and magnetite-chromite (Ziemiak & Castelli, 2003). Most commonly observed magnetic
Variation of the Curie temperature for four sets of binary systems. Fe₃O₄–(Fe,Mg)₂SiO₄ (Kontry et al., 2004; Yamamaka & Okita, 2001); Fe₃O₄–Al₂MgO₄ (Harrison & Putnis, 1996; Nishitani, 1981); Fe₃O₄–Fe₂TiO₄ (Lattard et al., 2006); Fe₃O₄–Cr₂FeO₄ (Ziemniak & Castelli, 2003).

Figure 9. Variation of the Curie temperature for four sets of binary systems. Fe₃O₄–(Fe,Mg)₂SiO₄ (Kontry et al., 2004; Yamamaka & Okita, 2001); Fe₃O₄–Al₂MgO₄ (Harrison & Putnis, 1996; Nishitani, 1981); Fe₃O₄–Fe₂TiO₄ (Lattard et al., 2006); Fe₃O₄–Cr₂FeO₄ (Ziemniak & Castelli, 2003).

In terrestrial solid-solution series is titanomagnetite with two end-members of magnetite (Fe₃O₄) and ulvöspinel (Fe₂TiO₄). A linear Tc estimation is successful in titanomagnetite series because Tc varies (relatively) linearly as a function of Ti content for Fe₂O₃–Fe₂TiO₄ series (e.g., Lattard et al., 2006; Pearce et al., 2010). In this series, both magnetite and ulvöspinel are inverse spinels. Three other solid-solution series are quite different in a sense that fayalite or forsterite, spinel, and chromite are all normal spinel. As the Group B spinels contain insignificant amount of Si, magnetite-fayalite or magnetite-forsterite is irrelevant to this study. Then, the Group B spinels can be approximated as a combination of magnetite-chromite and magnetite-spinel systems, although magnetite-chromite has our preference on the basis of compositional similarity (Figure 6 and Table 3). It is fortunate that both magnetite-chromite and magnetite-spinel systems display similar trends in Tc variation for x > 0.4 (Figure 9).

A simple linear mixing model between magnetite (Fe₃O₄; Tc = 580°C) and chromite (FeCr₂O₄; Tc = −180°C) predicts Tc ~ 100–200°C, about 50–150°C lower than our observation. There are three possibilities for the observed Tc being higher than the predicted Tc from a linear mixing model. First, a linear mixing model underestimates Tc due to an inherently complicated structural transformation of various spinel compositions (Francombe, 1957). A second possibility is the role of other minor elements. Both in terrestrial (e.g., Kumar & Bhalla, 1984a; Yu et al., 2001) and extraterrestrial Cr-rich spinels (e.g., Weiss et al., 2000, 2002, 2008; Yu & Gee, 2005), it is common to observe cations other than Cr and Fe. In general, Curie temperature of magnetic spinel is inversely proportional to the increment of Al substitution (Özdemir & Moskowitz, 1992). In the present study, the Group B spinel shows less than 10% contribution from metal cations without unpaired electrons of Al and Mg and Mn (Figure 6 and Table 3). Third, oxidation in the spinel by raising z can enhance the Tc. For instance, ordering temperature of chromite is quoted to rise from 70 to 520 K with increasing z (Schmidbauer, 1987).

4.4. Serpentinization-Related Magnetizations of Cr-Rich Spinel

Compositional constraints may be used to determine the presence of magnetic Cr-rich spinel. Despite the limited number of our data set, an important compositional condition for the presence of magnetic Cr-rich spinel can be quantitatively proposed. For instance, analysis from the ternary diagrams indicates that Cr-rich spinel is magnetic when the amount of metal cations without unpaired electrons (Al and Mg combined) is confined to less than 10% (Figure 6). In addition, magnetic Cr-spinel has a cation ratio of [Cr]/[Fe²⁺ + Fe³⁺] ranging from 1.33 to 1.56 (Table 3). At the same time, magnetic Cr-rich spinel occurs within the serpentine seams developed along the massive olivine grains (Figures 4 and 5). Then it is likely that magnetic Cr-rich spinel is a secondary phase associated with metasomatic alteration. Despite its highly refractory behavior, chromite rarely preserves its original magmatic textures. In reality, multiple stages of hydration-induced growth of serpentines occur at the expense of the primary anhydrous assemblage of olivine (or pyroxene), while chromite experiences textural changes and chemical alteration (Grieco & Merlini, 2012). Overall, the existence of magnetic Cr-rich spinel requires specific compositional conditions including a cation ratio of [Cr]/[Fe²⁺ + Fe³⁺] from 1.33 to 1.56 as well as a low oxide ratio of (Al₂O₃ + MgO)/(Cr₂O₃ + FeO + Fe₂O₃) less than 10% (Figure 6). Such conditions are available for ultramafic bodies formed in intraoceanic island arcs or in some continental mantle lithosphere (Figure 7).

Sum of total unpaired spins (STUS) for each spinel composition is calculated (Table 3). The spin-only dipole moment is 3 μB for Cr³⁺ (15²s²²p⁶³s³⁶p⁶⁴s²³d⁶), 4 μB for Fe²⁺ (15²s²²p⁶³s³⁶p⁶⁴s²³d⁶), 5 μB for Fe³⁺ (15²s²²p⁶³s³⁶p⁶⁴s²³d⁵), and 5 μB for Mn²⁺ (15²s²²p⁶³s³⁶p⁶³d⁶) where 1 μB (=9.274 × 10⁻²⁴ Am²) is the Bohr magneton produced by an unpaired electron spin. Due to their electron configurations, Mg²⁺ (15²s²²p⁶³s³⁶p⁶²d⁶), Al³⁺ (15²s²²p⁶³s³⁶p⁶²d³), Si⁴⁺ (15²s²²p⁶³s³⁶p³), Ca²⁺ (15²s²²p⁶³s³⁶p³⁶d³), and Ti⁴⁺ (15²s²²p⁶³s³⁶p³⁶d³) have no spin-only dipole moment. The STUS for Group A, Group B, and Group C spinel is 109.2–110.2, 72.4–76.3, and 38.6–53.1, respectively (Figure 10a and Table 3). It is evident that the STUS shows a significant correlation with the cation ratio of [Fe²⁺]/[Fe³⁺ + Cr³⁺] except for RA-C2 which is extremely Fe²⁺ deficient (Figure 10a). A simple mixing of spinel end-members can be used to interpret the compositions of magnetic Group B Cr-rich spinel. Observed compositions of magnetic Group B Cr-rich
spinel can be decomposed as 1/16 spinel (=MgAl₂O₄), 2/16 magnesioferrite (=MgFe₂O₄), and 13/16 chromite (=FeCr₂O₄). Such decomposition predicts a STUS of 75 for Group B spinel, consistent with the estimated STUS (Table 3). It is possible that there is a minimum value of 72.8 in the STUS for Cr-rich spinels to be magnetic (Figure 10a).

The magnetic versus nonmagnetic behavior is somewhat predictable from the degree of serpentinization inherited from the tectonic origin of ultramafic bodies (Figure 10b). The nonmagnetic samples are all from layered-mafic intrusions (CR) (Raedeke & McCallum, 1984) or Fe-deficient ophiolite complexes (LE1, LE9, RA) (Moutte, 1982; Pedersen et al., 1993). The magnetite-bearing samples (MO, PE, PY; alpine peridotites) brought up during orogenic events (e.g., Kamei et al., 2010; Le Roux et al., 2007; Medaris et al., 1990) or from the remnants (TR) of back-arc oceanic lithosphere (e.g., Gruau et al., 1991). The rocks with magnetic Cr-rich spinel are from continental mantle lithosphere (AL) (e.g., Kostenko et al., 2002; Lappin, 1974) or chromite pods/deposits (MA) (e.g., Lago et al., 1982). The Twin Sister (TW) ultramafic complex also contains magnetic Cr-rich spinel, although its exact origin is unknown (e.g., Toy et al., 2010). The TW sample is from an area that was deformed at lithospheric mantle conditions of ~800°C based on two-pyroxene and olivine + spinel geothermometry (Tikoff et al., 2010). The mixed magnetite/magnetic Cr-rich spinel sample is from Cypress Island ultramafic complex (Fidalgo ophiolite) of Jurassic age, interpreted as forming in an intraoceanic island arcs settings and subsequently carried on thrust sheets during a terrane collision (Whetten et al., 1980).

We can constrain the origin of NRM in our Group A and Group B spinel phases using the degree of serpentinization (Figure 10b). It can be proposed that the magnetic remanence carrier reflects the degree of low-temperature metamorphism (serpentinization). The best experimental evidence that favors our proposition is the presence of magnetite along the fractures between/among olivine grains in severely serpentinized rocks (CY, MO, PE, PY, and TR). Hence, it is unlikely that NRM for CY, MO, PE, PY, and TR is a
thermoremanent magnetization (TRM). Furthermore, serpentinization is a low-temperature hydrothermal metamorphic process that occurs at 150–300°C (Frost & Beard, 2007), well below the Curie point of magnetite. Then, NRM is more likely a chemical remanent magnetization (CRM) or a thermochemical remanent magnetization (TCRM). In samples CY, MO, PE, PY, and TR, NRM is acquired as a result of strong metasomatic reaction associated with serpentinization in the subduction-induced metamorphism of ultramafic complexes. By contrast, magnetic Cr-rich spinel from the least serpentinized ophiolites (e.g., MA, TW) or ultramafic complexes (e.g., AL, TW) lacks heavy serpentinization. Distribution of magnetic Cr-rich spinel along the fractures of silicates (mostly olivine) may support a CRM or TCRM origin of the NRM. However, considering the weakly metamorphosed characteristics in addition to the low Curie point, a TRM origin of the NRM cannot be completely ruled out.

5. Conclusions

1. This study was designed to demonstrate that intermediate compositions of Cr-rich spinels collected from serpentinized ultramafic complex are capable of carrying a stable remanent magnetization. We prepared 12 samples that might contain potentially magnetic Cr-rich spinel. According to demagnetization data, eight samples are magnetic, while four other samples are paramagnetic. On the basis of chemical compositional analysis and physical magnetic behavior, three different opaque phases were identified as Group A Fe-rich spinel, Group B Cr-rich spinel, and Group C Cr-Al-rich spinel. NRM of Group B spinel varies from 2.07 × 10⁻⁷ to 1.39 × 10⁻⁶ Am². NRM of Group A spinel ranges from 3.21 × 10⁻⁶ to 6.04 × 10⁻⁶ Am², except for the highest NRM (CY2-AF, CY2-T) of 2.05–2.75 × 10⁻⁴ Am².

2. The Group A spinel (i.e., magnetite) is responsible for the main NRM in severely serpentinized samples, which are collected from intraoceanic island arcs, orogenic exposures of ultramafics, and back-arc continental lithosphere. Magnetic Group B Cr-rich spinel shows maximum unblocking temperatures of 200–280°C, permitting remanence at depths of up to 8–12 km in terrestrial lithospheres assuming a geothermal gradient of 25 K/km. Compositional data indicate that Cr-rich spinel is magnetic when a cation ratio of [Cr]/[Fe²⁺ + Fe³⁺] ranges from 1.33 to 1.56 and a oxide ratio of (Al₂O₃ + MgO)/(Cr₂O₃ + FeO + Fe₂O₃) remains lower than 0.1. Magnetic Group B spinels are observed for ultramafic bodies formed in intraoceanic island arcs or in some continental mantle lithosphere settings.

3. The Group A spinel occurs mainly along the fractures between/among olivine grains in heavily serpentinized rocks. Both compositional analysis and microscopic observations indicate that spinels in Groups B and C seem to experience metasomatic or hydrothermal alteration during serpentinization. Overall, it is evident that compositions of spinels are related with the degree of serpentinization in ultramafic bodies.

4. Magnetic Cr-rich spinel can acquire stable remanence as a result of the subduction-induced metamorphism of ultramafic complexes. Distribution of magnetic Cr-rich spinel along the fractures of silicates (mostly olivine) may support a chemical origin of the NRM.

Data Availability Statement
Data availability is described online (at https://figshare.com/s/3f32e920161166df50607).

Conflict of Interest
The authors declare that they have no competing financial interests.

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