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### Short Communications

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Short Communication

**Oxidization of the mantle caused by sediment recycling may contribute to the formation of iron-rich mantle melts**

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Mantle-derived primary magmas generally have  $\text{FeO}^{\text{tot}}$  contents of about 11 wt.%. However, some primary melts show extremely high  $\text{FeO}^{\text{tot}}$  (>13 wt.%) with high MgO (> 12 wt.%) (ferropicrite) [1]. Considering the influence of chemical and mineral compositions of the mantle source on melt compositions, it has been argued that ferropicrites may be near-primary partial melts of pyroxenite formed in the convecting mantle [2-4], whereas others favor an origin by partial melting of an iron-rich peridotitic mantle source [5, 6]. Melting experiments have shown that melting conditions such as pressure and temperature can strongly influence the melt compositions, such that ferropicrites may be generated by partial melting of an olivine-dominated mantle source at ~5 GPa [5]. Some ferropicrites seem to be more oxidized than other magmas, as suggested from the Panzihua intrusions in the Emeishan large igneous province [7], which may imply melting of a more oxidized mantle source. Furthermore, Johnston and Stout [8] showed that oxygen fugacity exerts great control on the compositions and stabilities of Cr-Fe-rich minerals, and may therefore significantly affect mantle-derived melt compositions. Local oxygen fugacity ( $f\text{O}_2$ ) and solidus temperature of the mantle can be dramatically affected by recycled sedimentary carbonates. This raises the question as to whether sedimentary carbonate recycling could have indirectly contributed to the formation of iron-rich melts in the mantle.

Here, we report magnesioferrite-bearing peridotite xenoliths from the Dalihu Neogene basalt and demonstrate that the recycling of sedimentary carbonate into the mantle can induce a high- $f\text{O}_2$  environment, and that partial melting of peridotite or pyroxenite in high- $f\text{O}_2$  conditions may produce iron-rich melts.

The Dalihu Neogene basalt is located in the Inner Mongolia–Daxinganling Orogenic Belt (IMDOB) (Fig. S1 online), which is the eastern extension of the Central Asian Orogenic Belt (see Appendix for detailed geological setting). Volcanic activity at Dalihu began approximately 15 Myr ago and continued to as recently as 0.16-0.19 Ma. In addition to the peridotite xenoliths investigated here (Fig. 1), the Dalihu basalts also contain abundant carbonatitic xenoliths that record recycling of sedimentary carbonate rocks to deep mantle [9]. Seven lherzolite xenoliths are studied here: they are mainly composed of olivine (Ol) (~50%), orthopyroxene (~Opx) (30%), clinopyroxene (Cpx) (15%) and spinel (Sp) (5%). Two types of olivine were identified in these peridotites, one

has normal Mg# (100Mg/(Mg+Fe)) for mantle olivine (90.5-91.0) and contains no exsolution (Fig. S2 online), while the other contains abundant exsolution lamellae of Fe-Mg-Ni oxides (Fig. 1b, c) and has appreciably higher Mg# (95.2-98.1) (Table S1 online). The high Mg# of olivines that bear exsolution lamellae correlates positively with the abundance of exsolutions (Fig. 1c, d). Magnesioferrite-rich spinels and hematite with extremely high  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio ( $>0.95$ ) were identified, and generally coexist with the high Mg# olivine (Fig. 1b, c). The magnesioferritic spinels occur as co-existing Mg-rich and Fe-rich end members [  $(\text{Mg}_{0.88}\text{Fe}_{0.10}\text{Mn}_{0.01}\text{Ni}_{0.01})_{1.00}^{2+}(\text{Fe}_{1.85}^{3+}\text{Al}_{0.13}\text{Cr}_{0.01})_{1.99}^{3+}\text{O}_4$  and  $(\text{Ni}_{0.54}\text{Mg}_{0.40}\text{Fe}_{0.06})_{1.00}^{2+}(\text{Fe}_{1.88}^{3+}\text{Al}_{0.10}\text{Cr}_{0.01})_{1.99}^{3+}\text{O}_4$  ]. Hematite has ~3% wt.%  $\text{Al}_2\text{O}_3$  with minor Cr and Mg (Table S1 online). Clinopyroxenes fall into two groups with differing Sr isotopic character: those with high Sr content show homogeneous and low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, whereas clinopyroxenes with low Sr content show variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio from core to rim (Fig. S3, Table S2 online, see Appendix for Methods).

(1) Mantle oxidization induced by sedimentary carbonate recycling. The extremely Mg-rich olivine may result from the exsolution of iron in a high  $f\text{O}_2$  environment [8, 10], Fe-Mg exchange between olivine and other phase [11], or it may be inherited from high-Mg# materials such as metamorphosed serpentine [12]. Olivines in the Dalihu peridotites generally have Mg# of 90.5-91.0, and no serpentine (or other high Mg# mineral) occurs, indicating that the Mg-rich olivine most probably resulted from a local high- $f\text{O}_2$  mantle environment rather than from the transformation of high-Mg# minerals. Furthermore, magnesioferrite ( $\text{MgFe}_2\text{O}_4$ ) is a rare mineral of the spinel group, and generally exists under oxidized conditions. The coexistence of Mg-rich olivine and high- $\text{Fe}^{3+}/\Sigma\text{Fe}$  phases in the Dalihu peridotite, and the intergrowth of magnesioferrite and hematite [13] thus records a strongly oxidized environment. Subsolvus oxidation of olivine converts  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ , which cannot fit in the octahedral site of olivine, resulting in the exsolution of magnesioferrite and hematite and an increase in the Mg# of the remaining olivine. This has been demonstrated experimentally to occur through reaction with infiltrating carbonate melts [14].

The carbonatitic xenoliths carried by the Dalihu basalt retain the trace element patterns and  $\delta^{18}\text{O}_{\text{SMOW}}$  values of argillaceous limestone, suggesting an origin by subduction of carbonate-rich sediments from the surface into the mantle [9]. Since

carbonate-rich sediments generally have much higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than mantle peridotites, the clinopyroxenes formed by the reaction between carbonate melts and peridotites should track this recycling because clinopyroxenes sequester most of the Sr in peridotites.

Although most clinopyroxene grains preserve the homogeneous and low  $^{87}\text{Sr}/^{86}\text{Sr}$  of the original mantle rock, some grains show increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from core to rim caused by reaction with infiltrating recycled sedimentary carbonate melts (Fig. S3 online). Subducted carbonate-rich sediments can potentially increase the  $f\text{O}_2$  of surrounding mantle during reduction of carbonate to graphite, or by the addition of  $\text{CO}_2$  fluid that results from decarbonation. It is thus reasonable to speculate that the extremely oxidized environment recorded by the peridotite could have been caused by the subduction of sedimentary carbonate.

(2) Origin of iron-rich mantle melts in high  $f\text{O}_2$  conditions. To simulate the chemical compositions of mantle-derived melts formed in oxidized conditions, partial melting of peridotite and pyroxenite under various high  $f\text{O}_2$  conditions (from QFM +0 to QFM +3) (Fig. 2) were modelled using pMELTS [15]. Since ferropicrite is associated with continental flood basalt provinces [2], which are resulted from the plume-type active upwelling, isentropic decompression melting model was used. Primitive mantle, depleted mantle, the Dalihu peridotites and the Hannuoba pyroxenites were used as source materials; detailed modeling information is described in the Appendix. Our modeling results show that melt compositions are strongly affected by  $f\text{O}_2$ , and show high  $\text{FeO}^{\text{tot}}$  and MgO at high  $f\text{O}_2$ . Generally, the  $\text{FeO}^{\text{tot}}$  and MgO contents of melts increase with increasing  $f\text{O}_2$  (Fig. 2a, b). Peridotite-derived melts have  $\text{FeO}^{\text{tot}}$  of 12.6 wt.%-13.6 wt.% at QFM+1, which increase sharply to about 16 wt.% at QFM+2.75 (Fig. 2a); Pyroxenite-derived melt has  $\text{FeO}^{\text{tot}}$  about 15 wt.% at QFM+1: this also increases sharply to 16 wt.% at QFM+2.75. Both modal olivine percentage in residue phases and the iron content in olivine decrease sharply with increasing oxygen fugacity (Fig. 2c), these may be the reason why  $\text{FeO}^{\text{tot}}$  in melt increases with increasing  $f\text{O}_2$ .

The high  $\text{FeO}^{\text{tot}}$  and MgO of primitive melts produced at high  $f\text{O}_2$  agrees well with the compositions of ferropicrites ( $\text{FeO}^{\text{tot}} >13$  wt.%, MgO ~19 wt.%) [5]. Although the oxygen fugacity of primary ferropicrite is rarely constrained, the high  $f\text{O}_2$  indicated by

high-Ti basalts from the Emeishan large igneous province [7] implies that the mantle source of some ferropicrite may be oxidized as well. This implies that ferropicrite could be produced by the partial melting of oxidized mantle peridotite, and that a Fe-enriched mantle source [1] is not necessary. Some pyroxenite-derived melts formed at normal mantle  $fO_2$  may have higher  $FeO^{tot}$  than melts of peridotite, and have been advocated to explain ferropicrite petrogenesis [4]. However, the  $Al_2O_3$  contents (about 14 wt.%) (Tables S3, S4 online) of these melts are much higher than in ferropicrites (<10 wt.%) [5]. Nevertheless, melting of pyroxenite under high  $fO_2$  may overcome this inconsistency and produce melts with high  $FeO^{tot}$ , MgO and low  $Al_2O_3$  contents that agree well with natural ferropicrites (Fig. 2). Overall, our *pMELTS* modeling shows that melting of mantle composed of a mixture of peridotite and pyroxenite under oxidized conditions may explain the formation of iron-rich mantle melts, particularly ferropicrites. The origin of the oxidized conditions may be related to the subduction of carbonates, *as suggested by our natural peridotite xenoliths*.

### **Conflict of interest**

The authors declare that they have no conflict of interest.

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### **Author contributions**

Yongsheng Liu designed the project. Detao He, Yongsheng Liu, Stephen Foley and

Mihai N. Ducea wrote the paper. Measurements were done by Detao He. All authors contributed to discussions and interpretations.

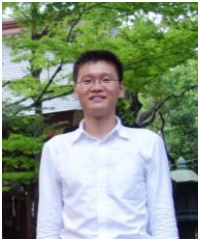
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**Figure captions:**

**Fig. 1 Micrographs of the Dalihu peridotite.** (a) Thin section of peridotite xenolith showing red, oxidized rims to olivines. (b, c) SEM pictures showing the occurrence of high Mg# olivine and high-Fe<sup>3+</sup> phases – bright lines and spots are magnesioferrite-rich spinel and hematite. Yellow circles are analysis spots with analysis spot numbers: see Table S1 (online) for corresponding analytical results. (d) Correlation between olivine Mg# and abundance of exsolutions of high-Fe<sup>3+</sup> phases. Stippled line is trend line. Mfr: magnesioferrite; Hem: hematite; Ol: olivine; Sp: spinel; Opx: orthopyroxene; Cpx: clinopyroxene; Mfr-Hem: Intergrowth of magnesioferrite and hematite.

**Fig. 2 (Color online)** Results of pMELTS calculations when pressure is 2.0 GPa. Variations of FeO<sup>tot</sup> (a), MgO (b) content in partial melts of peridotite and pyroxenite as function of  $fO_2$ . (c) Variations of modal olivine percentage in residue phase and FeO<sup>tot</sup> content in olivine from primitive mantle as function of  $fO_2$ . The FeO<sup>tot</sup> content of primary melt of Parana-Etendeka ferropicrite (solid line) and picrite (dashed line) are also shown for comparison [5]. See appendix for data sources and detailed explanation.

