Trace element of titanomagnetite in layered mafic-ultramafic intrusions: implications for oxide ore genesis

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Titanomagnetite has always been considered as a late crystallizing phase from basaltic magma. Precipitation of titanomagmetite is usually initiated after a lengthy period of fractionation of olivine and plagioclase, which has been proved to increase both the Fe content and the oxygen fugacity of the evolving magma [1]. However, early saturation of Fe-Ti oxides was proposed because of the occurrence of abundant Fe-Ti oxide inclusions in olivine and plagioclase [2]. In this study, we carefully examine the distribution, microtexture and chemical composition of Fe-Ti oxide minerals of Baima Fe-Ti oxide deposit in Emeishan Large Igneous Province, Southwest China. Titanomagnetite occurs as interstitial phase coexisting with a minimum amount of sulfides (Fig. 1a), or as droplet enclosed in olivine with/without other mineral assemblage (Fig. 1b, c). The major element compositions of titanomagnetite determined by electonic microprobe are highly variable, partially due to the extensive exsolution of ilmenite and spinel. Trace elements, including Ti, Zn, Cr, V, Mg, and Ni, are dertermined using in situ LA-ICP-MS. These datsets are compared with those of bulk compositions of oxide separates. From this study, the evolution stage of differentiation of titanomagnetite is revealed [3]. Combining with petrography of the oxide ores, the new dataset indicates that titanomagnetite formed from immiscible Fe-Ti-(P) melts in silicate magmas. From these immiscible melts, sulphur was saturated, resulting in the formation of sulfide blebs in oxide ores.

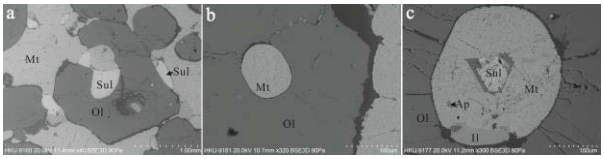

Figure 1: Titanomagnetite occurring as net-textured mass (a) or inclusions in olivine (b, c). Sul-sulfide, Mt-titanomagnetite, Ol-olivine, Ap-apatite, Il-ilmenite.

[1] Reynolds (1985) *Econ. Geol.* **80**, 1089-1108. [2] Pang (2008) *CMP* **156**, 307-321. [3] Duchesne (1999) Miner Depos 34, 182-198.

Theoretical calculations of equilibrium clumped isotope signatures beyond harmonic approximations

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Clumped isotope geochemistry studies isotope distribution of isotopologues containing more than one rare isotope which could provide unique information such as formation temperatures of geological events. The measurement of clumped isotope signatures in laboratory needs calibration between observed isotopic data and formation temperatures in order to take account isotope fractionations in experimental procedures. One method of calibration is to measure the clumped isotope signatures of temperature-known materials to scale the temperature curve made of experimental data. Theoretical calculation using quantum chemistry methods could also become a powerful tool to study clumped isotope signatures. However, the precision required for clumped isotope calculation is very high. Theoretical treatments beyond harmonic approximations are therefore highly recommended.

In this study, theoretical treatments beyond the harmonic level by including several higher-order corrections to the Bigeleisen-Mayer equation are used to predict accurate Δ_i and Δ_{mass} results for ^{13}C-^{18}O and ^{13}C-^{2}H (or ^{13}C-D) clumps in carbonates and organic compounds. The details of these higher-order corrections can be found in [1]. Our preliminary results suggest significant improvement on the calculation of ^{13}C-D clumped isotope fractionations.

[1] Liu et al. (2010) *Geochim. Cosmochim. Acta* **74**, 6965-6983.