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V/Sc in garnet xenocrysts: new oxybarometry frontiers for the SCLM

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Introduction

The oxidation state of the subcontinental lithospheric mantle (SCLM) is often estimated by measurements of oxygen fugacity (fO_2) using methods such as Mössbauer Spectroscopy or XANES to measure Fe^{3+}/Fe^{2+} in mantle xenoliths. While precise and accurate, these approaches can be limited by the availability of equipment or samples (e.g., weathered environments); thus, the development of alternative redox proxies is desirable. As peridotitic garnets can carry elements such as V and Cr with differences in valence states and partition coefficients, easily determined by EMP or LA-ICP-MS, Cr-pyrope xenocrysts often recovered in heavy mineral concentrates become a suitable monomineralic fO_2 proxy.

In this contribution, we evaluate V/Sc in garnet (V/Sc_{gnt}) as a new oxybarometer for SCLM domains. We investigate how oxygen fugacity and other factors such as element partitioning, temperature, pressure and metasomatism might affect the V/Sc trend in garnets from lithospheric domains representing various tectonothermal age ranges (i.e., Archon (A), Proton (P), Tecton (T) and their combinations; see Begg et al., 2009).

Calibrating the V/Sc_{gnt} redox proxy

The V/Sc ratio is a function of fO_2 assuming that the compatibility of V valence states (V^{2+} to V^{5+}) in key mantle-derived minerals such as garnet, spinel and clinopyroxene controls the partitioning coefficient (D) behavior between silicate/oxide phases and melts. Changes in fO_2 conditions during the melting of peridotites, along with minor effects of temperature (T), pressure and composition, reflect the sequence $D^{garnet/melt}{}_{V3+} >> D^{garnet/melt}{}_{V4+} > D^{garnet/melt}{}_{V5+}$. In contrast, the partition coefficient of the monovalent Sc (Sc^{3+}) is constant ($D_{Sc}{}^{grt/melt} = 6$) and generally only affected by compositional variation rather than fO_2 variations (Mallmann and O'Neill, 2007; 2009).

Partitioning data from cratonic peridotite xenoliths show that V/Sc_{gnt} increases due to the higher uptake of V^3 in garnet as temperature rises and fO_2 drops; when the value reaches ~3, the trend is near constant at any T. The locus of the maximum V/Sc_{gnt} with increasing T, expressed as $V/Sc_{max} = 0.007(T - 600°C)$, is defined as the Craton Reference Line (CRL) (Fig. 1a). The projection of V/Sc_{max} onto the upper limit defined by known ΔFMQ values for cratonic xenoliths (Fig. 1b), then defines the maximum oxygen fugacity ($fO_2{}^{max}$) in typically depleted cratonic SCLM. At the deepest levels, the minimum fO_2 approaches the Iron-Wüstite buffer (IW).

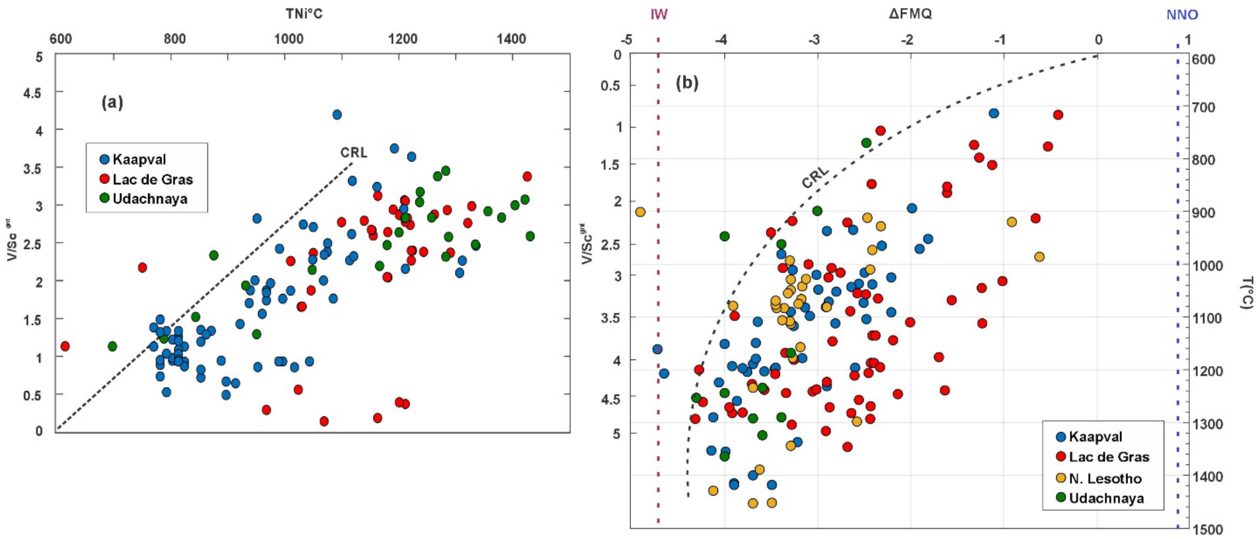

Figure 1. Compilation of cratonic garnet peridotite xenoliths (Yaxley et al., 2017 and references therein) as a function of temperature: (a) V/Sc_{gnt} vs TNi for garnets, defining the CRL; and (b) Oxygen fugacity relative to ΔFMQ. IW and NNO buffers for reference.

Global trends

A comprehensive garnet xenocryst dataset representing well-studied SCLM worldwide (Chassé et al., 2018) was used to analyse V/Sc_{gnt} versus T_{Ni} (Ni-in-garnet thermometer; Ryan et al., 1996)

Most Archon localities (e.g., Group I kimberlites, Kaapvaal Craton; Fig. 1a) have V/Sc_{gnt} trends with upper limits on, or slightly above, the CRL, down to the inferred Base of the Depleted Lithosphere (BDL). V/Sc_{gnt} ranges from 2.5 to 3.5 for higher-T garnets reflecting melt-related metasomatism (ΔFMQ -3.5 to -4). Garnets from Proton/Archon terranes (e.g., Premier/Cullinan, Limpopo Belt; Gawler Craton) V/Sc_{gnt} usually show more scatter in V/Sc_{max}, but most define upper limits *ca* 0.5 V/Sc units below the CRL.

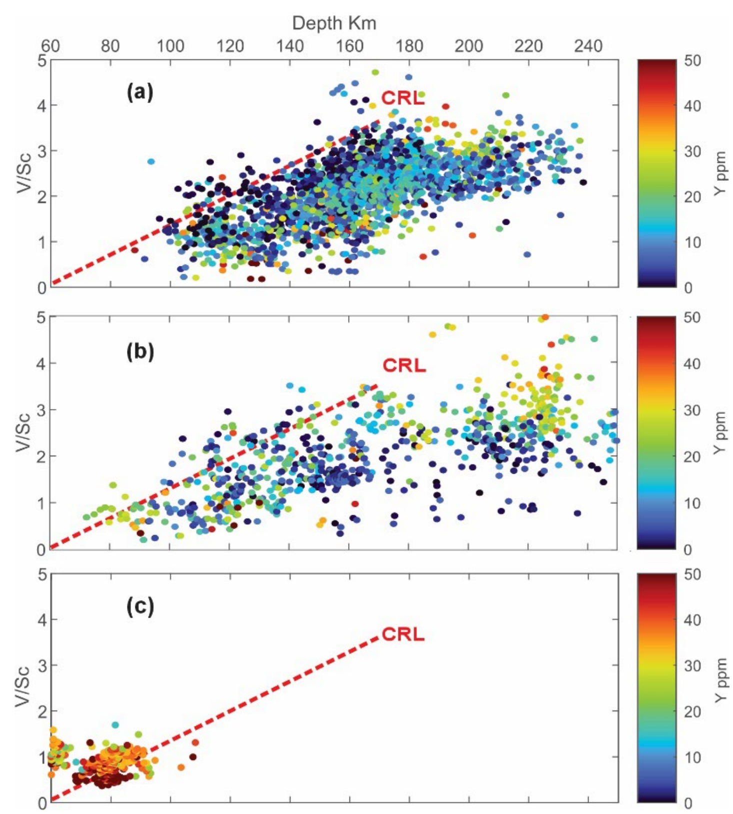

Figure 2. Data from (a) Archon, (b) Proton and (c) Tecton garnets plotted against depth, with variations in Y contents shown as a colour scale.

V/Sc_{gnt} from Tecton localities (e.g., Malaita, Tertiary basalts) is typically low at any T. In P/T and A/P/T terranes such as the SW São Francisco Craton, V/Sc_{gnt} trends typically lie above the CRL, particularly at low T, indicating a significantly lower fO_2 than that at similar depths in cratonic SCLM.

Implications

The defined CRL may represent the primordial distribution of fO_2 in a thick, highly depleted Archean SCLM (Yaxley et al., 2017). The calibration of V/Sc_{gnt} against the fO_2 data from cratonic xenoliths indicates that minimum values at the deepest levels approach the Iron-Wüstite buffer (IW), suggesting the influence of COH fluids from the metal-saturated sublithospheric mantle, dominated by methane (CH_4) and hydrogen. Minimum values of fO_2 increase upward through the SCLM, possibly reflecting the progressive partial oxidation of ascending CH_4-rich fluids. As SCLM peridotites have low buffering capacity, changes in fluid composition might effectively control the fO_2 at any depth, which is consistent with typically near-FMQ estimates for shallow spinel peridotite xenoliths.

In Archons, V/Sc_{gnt} trends mostly follow the CRL but the values from high-T garnets (Figs 1a, 2a) may reflect the prevailing fO_2 in the zone of melt generation near the base of the SCLM. Patterns from Proton/Archon (Fig. 2b) terranes appear to reflect the modification of pre-existing Archon SCLM, including oxidation, heating and metasomatic growth of clinopyroxene. Fertile Tecton garnet lherzolites (Fig. 2c) have near-FMQ values (V/Sc_{gnt} mean <0.5, ΔFMQ 0 to -1) that are mostly controlled by compositional variations. Lastly, the V/Sc_{gnt} trends in geologically complex terranes (P/T and A/P/T) suggest a reduction in fO_2 due to metasomatism during SCLM thinning, implying the continuous flow of reduced asthenosphere-derived fluids into the base of the thinned lithosphere.

V/Sc_{gnt} appears to be an effective tracker of fO_2 changes in the SCLM, and for evaluating the processes controlling oxygen fugacity in the SCLM.

References

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