

Limitations of magnesium isotope fractionation geothermometry determined using laser ablation

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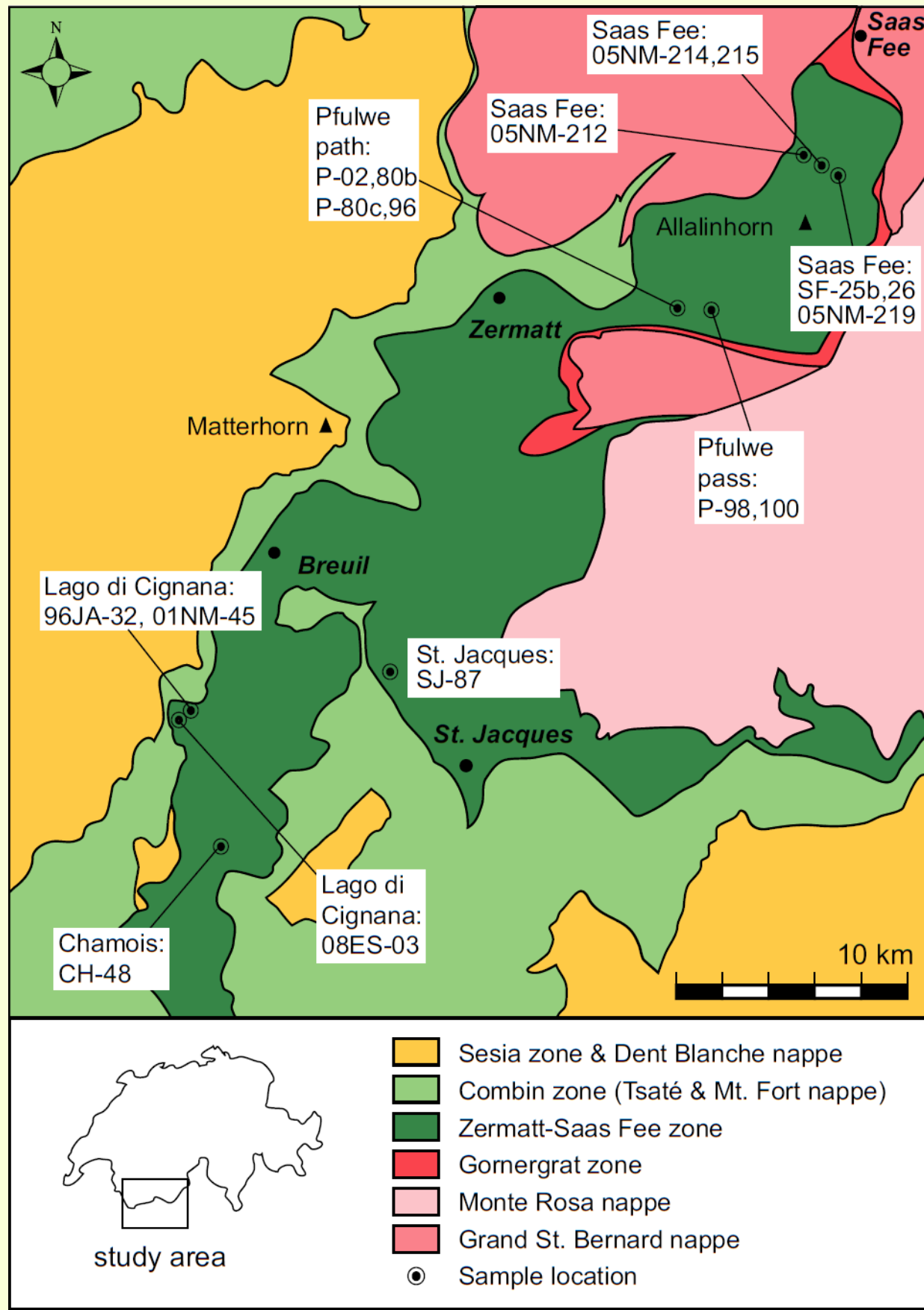
Introduction

The magnesium isotope fractionation during high-pressure, low-temperature metamorphism can be leveraged to constrain the formation environment of these rocks. Clinopyroxene more readily accepts heavier Mg isotopes into its cation site than garnet does; this substitution provides a record of temperatures experienced by the minerals. Eclogites, formed by subduction of basalts, comprises these minerals and have been the focus of studies utilizing this geothermometer. Pickles et al. (2016) and Li et al. (2016) have demonstrated that this geothermometer has sufficient temperature resolution to join the widely-used Fe-Mg exchange geothermometer.

Here, we examine the limitations of applying this method to the in situ analysis via laser ablation of an eclogite exhumed at Zermatt-Saas as a means of accounting for zoning and avoiding inclusions, which would cause inaccuracies in other methods of data collection. Elemental zoning was determined using electron microprobe analysis. Application of the Fe-Mg exchange geothermometer determined peak temperatures of 950°C at 24kbar, exceeding the range given by Angiboust et al. (2009) of 540°C ± 20°C at the same pressure. However, the thermal profiles determined matched those described by Skora et al. (2015) for this locale, prolonged prograde metamorphism followed by brief retrograde metamorphism. To facilitate a systematic comparison between the geothermometers, the temperatures suggested by the Fe-Mg geothermometer were converted to Mg isotope fractionation estimates using the calibrated equation from Li et al. (2016). Under laser ablation ICP-MS analysis of identical traces to the electron microprobe analyses, actual Mg isotope fractionations over a much wider and unreasonable range. This study serves to highlight the geometric problems presented by in situ LA analyses and the limitations of comparisons between the pressure-dependent elemental geothermometer, Fe-Mg fractionation, and the pressure-independent Mg isotope fractionation geothermometer.

Sample Description and Background

An eclogite exhumed at Zermatt-Saas, from the western Alps of Switzerland (see below), was selected for study. Other studies of eclogites from Zermatt-Saas have placed temperature constraints of 540 ± 20°C (Angiboust et al. 2009) to 650°C (Li, Rahn, and Bucher. 2004) and pressure constraints of 17.5-20 kbar (Barnicoat and Fry, 1985) to 23 ± 1 kbar (Angiboust et al. 2009). Zermatt-Saas Fee eclogites are omphatic, originally the basaltic Liguoro-Piemont Ocean basin that was closed at the end of the early Cenezoic (Skora et al. 2015) and thrust to the surface post-metamorphism. Notably, metamorphic retrogression has been noted in other eclogites from Zermatt-Saas Fee, characterized by Na-Ca rich rims of garnet, omphacite, and glaucophane (Skora et al. 2015). In addition, eclogites in the Saas Fee region display the peak metamorphic assemblage of any region in the western Swiss Alps (Skora et al. 2015.)



Map of Zermatt-Saas and surrounding geologic zones in the Swiss Alps. From Skora et al. 2015.

Omphacite, an intermediate clinopyroxene, comprises the matrix of the sample. The coarsest of these grains was nearly 1 ± .5 mm in diameter, but much of the matrix was much finer. Several large grains of glaucophane were present, reaching 2.5 ± .5 mm in diameter. Alteration of the omphacite matrix to jadeite was found around the glaucophane grains. Garnet grains are markedly poikiloblastic, frequently containing inclusions of glaucophane and omphacite; inclusions of rutile and titanite were present. The presence of silica was detected adjacent to garnet grains.

Geothermometry

The paragenesis of garnet (Grt) and clinopyroxene (Cpx) is typical in metamorphic rocks of mafic and ultramafic origin, particularly in the relatively low-temperature environment of subduction zones. Geothermometry and geobarometry of eclogites rely on the chemical exchanges within these mineral pairs as equilibrium is reached; a common technique utilizes the exchange of Fe2+ and Mg cations, but models using other exchanges, such as trace elements and their effects on lattice strain (Pickles et al. 2016), have also been developed. This study focuses on the inter-mineral isotope fractionation of solely the Mg cation in the respective minerals, controlled by the change in coordination number of the site between garnet and clinopyroxenes from 8-fold to 6-fold, respectively. While it is more energetically favorable for the heavier isotope (26Mg) to be included in the 6-fold site of clinopyroxene, this effect is mitigated as temperature increases.

The use of this magnesium isotope exchange for geothermometry, pioneered by Li et al (2011), has distinct advantages over other models. The Fe2+ and Mg content of minerals is typically determined via electron microprobe analyses, but requires correction via stoichiometric estimation of Fe3+, which can lead to inaccuracies (Li et al. 2011). The Fe2+ and Mg technique is limited in scope as well; it cannot be applied to rocks with high Ca content in the minerals of interest (Zhang et al 1996).

Isotope ratios are reported in δ-notation in per mil compared to BCR-2G, a basaltic glass standard, where X is the magnesium isotope in question (24, 25 or 26):

$$\delta^X\text{Mg} = \left[\frac{\left(\frac{^X\text{Mg}}{^{24}\text{Mg}} \right)_{\text{Sample}}}{\left(\frac{^X\text{Mg}}{^{24}\text{Mg}} \right)_{\text{BCR-2G}}} - 1 \right] * 1000$$

Fractionation between the mineral pairs is notated as:

$$\Delta^X\text{Mg}_{\text{Cpx-Grt}} = \delta^X\text{Mg}_{\text{clinopyroxene}} - \delta^X\text{Mg}_{\text{Garnet}}$$

Methods

Mapping of zoning in garnet and clinopyroxene via electron microprobe analysis

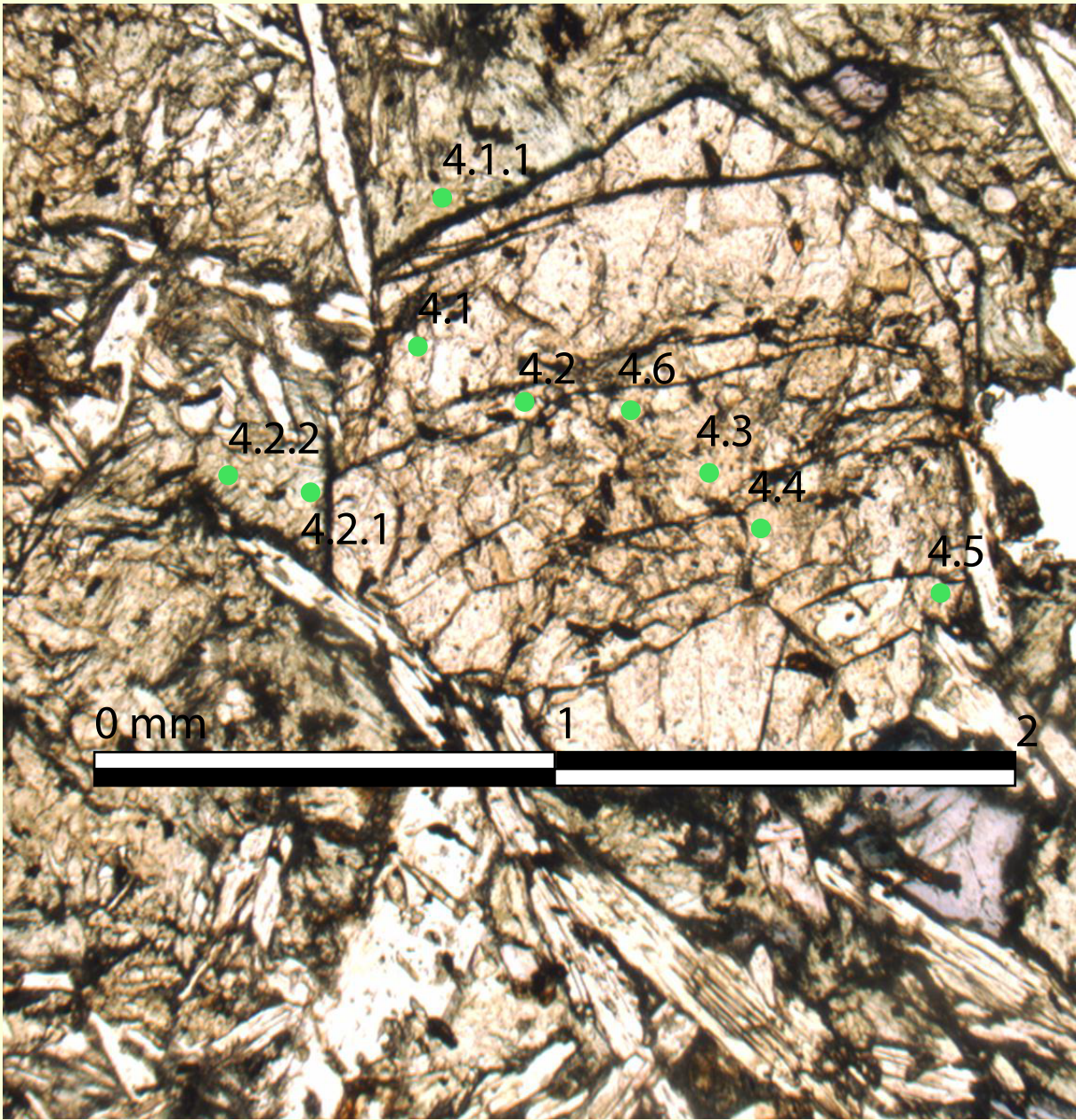
Major and minor element compositions of garnet and clinopyroxene grains were determined for discrete spots using the Jeol JXA-8900 electron microprobe at the University of Maryland, College Park. Operating conditions under wavelength-dispersive mode were 15 kV accelerating voltage, 10 nA beam current, and 5 μm beam diameter. Spot analyses between the core and rim of grains were performed at sub-equal distances to constrain the presence and nature of chemical zoning. All 6 garnet-clinopyroxene pairs were selected for EMPA analysis; a 15 point transverse was performed. Data containing no CaO or MgO were assumed to be an inclusion or fracture in the grain and was not reported.

In situ Mg isotope determinations by MC-LA-ICP-MS

The relative 24Mg, 25Mg, and 26Mg content of the clinopyroxene and garnet of the sample were determined with a low-resolution Nu Plasma multi-collector (MC) ICP-MS connected to the same New Wave 213 laser ablation system at the University of Maryland, College Park. Standard-sample collection bracketing was implemented to track fluctuations in measurement calibration. Identical conditions to the reference material analysis were used. The laser repetition rate was 7Hz under dry plasma conditions; a spot size of 40μm was selected to minimize the effect of coning as material is ablated. By mitigating coning, a longer collection time was able to be utilized. On each measurement, a minimum of 30 seconds was spent collecting background and a minimum of 60s was spent collecting isotopic signal. The MC-ICP-MS does not reach saturation at the spot size of 40μm; this saturation was the restricting factor on the spot size for the single-collector. Laser repetition frequency and spot size remained constant across standard and sample testing. For each section of bracketing, signal intensities of the Mg isotopes are to be measured in counts per second for an initial 30 seconds with the laser shutter closed to monitor background signal, followed by 60 seconds of ablation of the material. A cooling period of 120 seconds is provided between measurements.

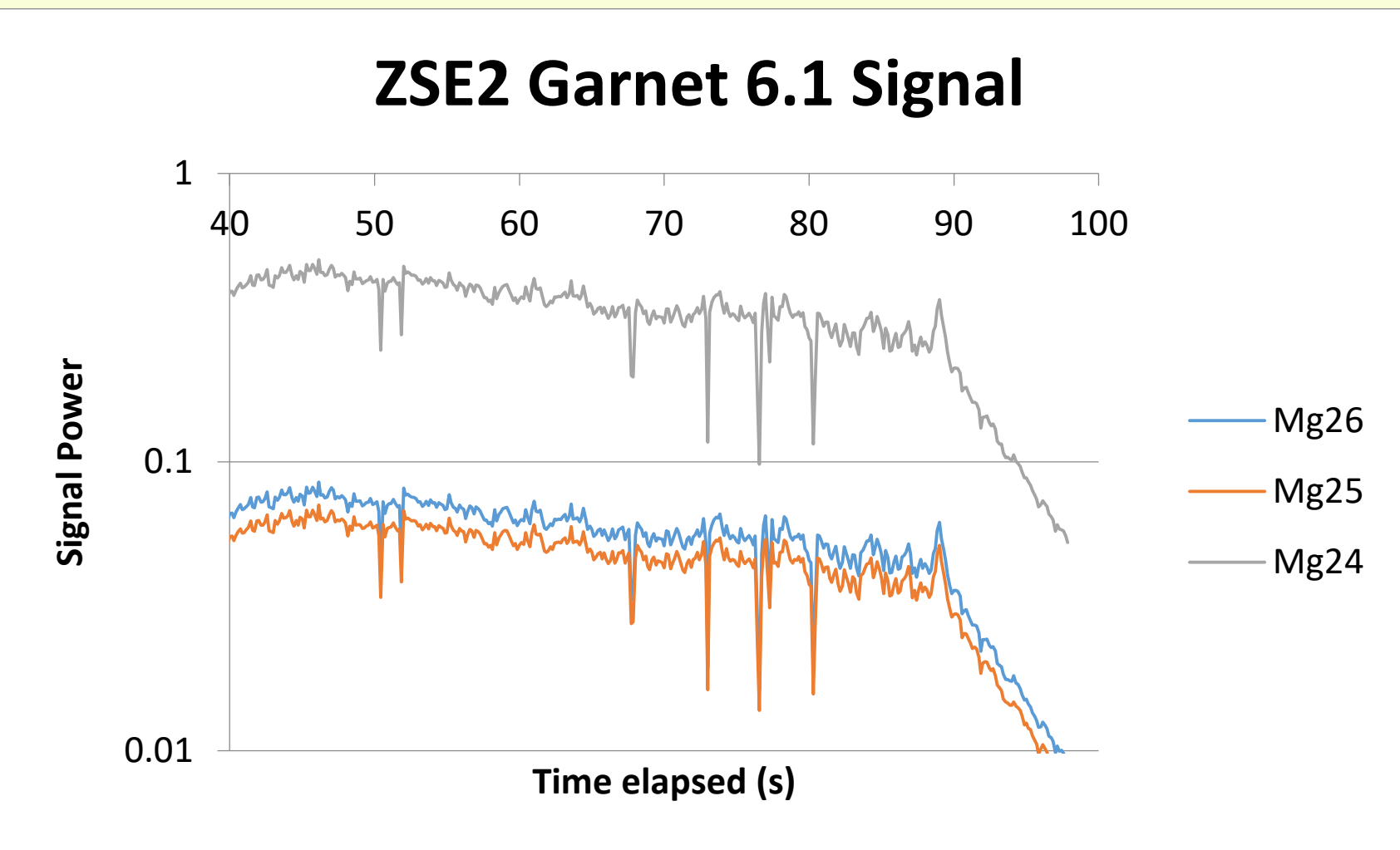
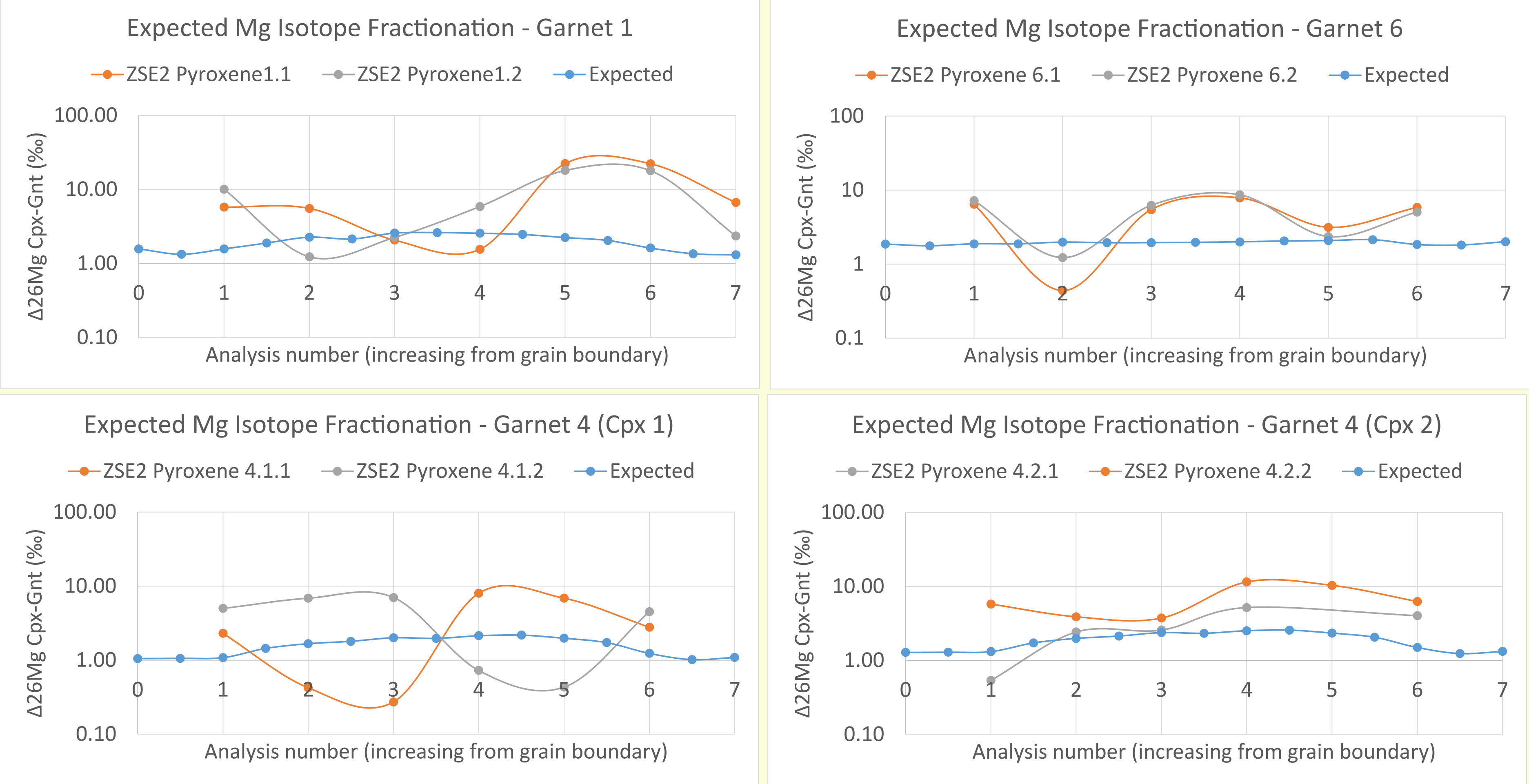
To process these measurements, a data reduction algorithm was used. Primarily, the algorithm differentiates background from measurement signal and evaluates the Mg isotope ratios at each cycle during measurement.

Plane-polarized map of garnet-clinopyroxene pairs 4.1 and 4.2:

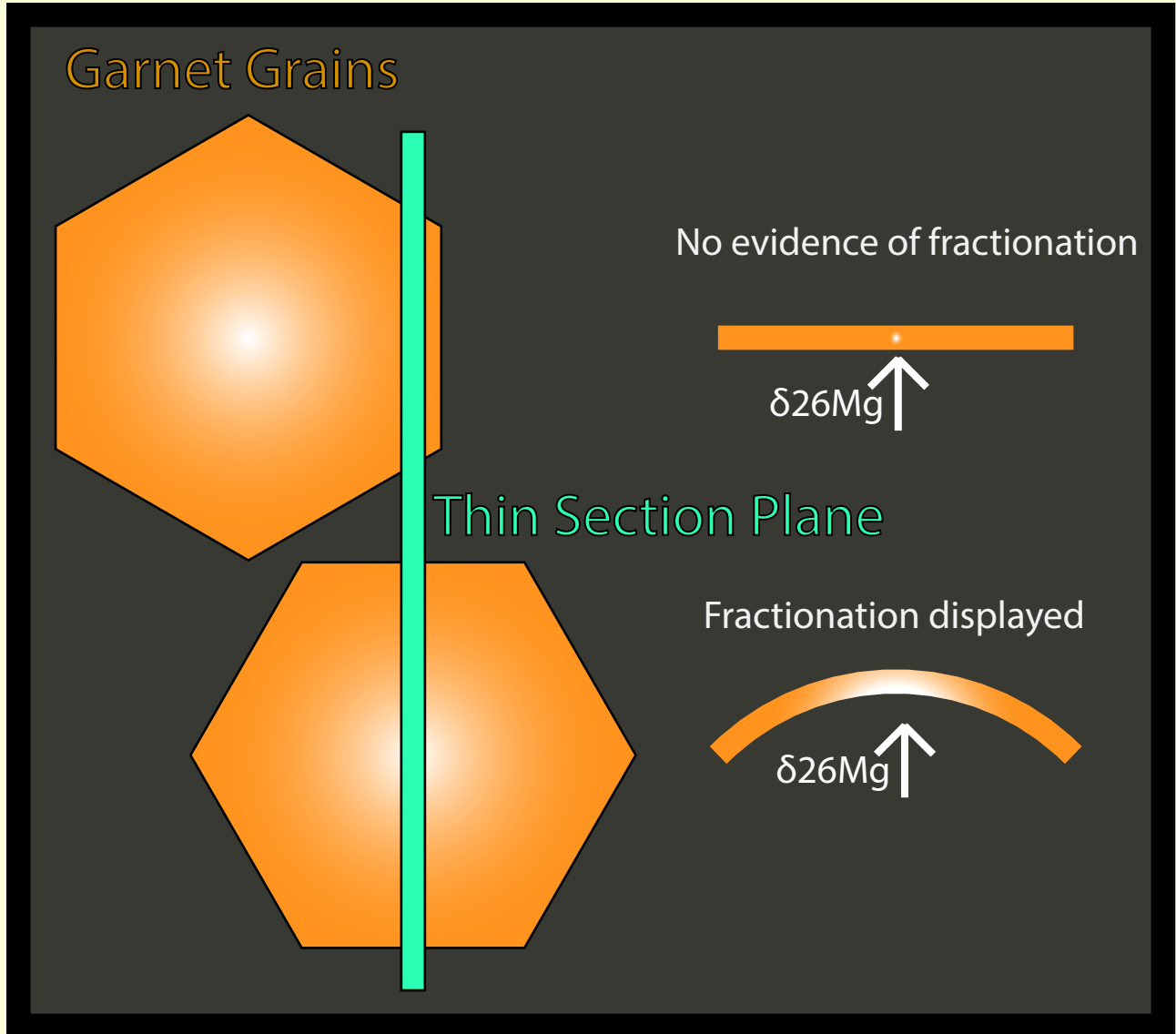


Results

In situ Fe and Mg measurements taken via EMPA were used as a method of evaluating the elemental zoning so that it could be compared to the isotopic Mg zoning. The Fe-Mg garnet-clinopyroxene geothermometer was applied to these measurements to form a comparison to the application of the Mg fractionation geothermometer to the LA-MC-ICP-MS Mg isotope measurements. Because both Fe-Mg and Mg isotopes fractionate into garnet and clinopyroxene as a function of temperature, I hypothesized a systematic relationship between the two fractionations would be evident. As discussed previously, both geothermometry applications agreed with the literature's description long prograde metamorphism followed by brief retrograde metamorphism (Skora et al. 2015). The Fe-Mg application's temperature determinations exceeded that described by the literature (Li, Rahn, and Bucher. 2004) by over a 300°C increase in the temperature of peak metamorphism. The Mg isotope geothermometer temperature determinations displayed an unreasonable temperature range, from a minimum -62°C to 1631°C. Garnet-pyroxene pair 6 was determined to have a high minimum temperature at the center upon application of the Fe-Mg geothermometer. Initially, this was assumed to be a result of the geometric limitation; the reduced fractionation at the center was not representative of the core of the mineral grain. However, this pair, 6, demonstrated the full range of temperature present in pair 1. In this case, pair 4.2 was determined to have the dampened temperature profile relative to the others, only displaying a peak temperature of 348°C (aside from one anomalous rim value). The pairs 6 and 4.2 best highlight the discrepancy between the temperature profiles described by each geothermometer.



Signal power of laser ablation MC-ICP-MS of Garnet 6, spot 1. Power decrease over time due to ablation coning.



Schematic diagram highlighting the geometric limitations of otherwise identical grains for in situ analyses.

Conclusion

Despite the apparent advantages presented by in situ analyses, the Mg isotope fractionation geothermometer has several limitations when applied to in situ data collection; in this case, laser ablation MC-ICP-MS was selected. There is an unavoidable geometric issue upon creating the thin section. The plane that passes through the mineral grains rarely cuts through the true core of the mineral grain. The effects of the laser system itself, including the coning and the possibility fractionation upon ablation of the mineral cannot be ignored either. The lack of pressure dependence is advantageous for determining the thermal profile experienced by minerals, but this limits any comparison with tools that are pressure-dependent, such as the Fe-Mg fractionation geothermometer. Another limitation proposed by Li et al. (2016), who developed the calibration of the Mg fractionation geothermometer, is that non-modal melting of eclogitic crust will result in additional light Mg isotopes in the garnet and therefore an underestimation of the temperature of formation.

However, developing this in situ application of the Mg isotope geothermometer is worthwhile. Avoidance of inclusions in poikiloblastic minerals is a necessary step in refining the accuracy of the tool; included minerals are unavoidable in dissolution analyses. The creation thermal profiles by analyzing isotopic fractionation from the core of mineral grains to the rim is a valuable asset in determining the metamorphic history of the rock. Additionally, this geothermometer is readily adaptable to similar mineral pairs, such as amphibole-garnet and biotite-garnet (Li et al. 2016).