



An empirical test of the crystal lattice strain model for rare-earth element partitioning into clinopyroxene

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ABSTRACT

The significance of crystallographic control over trace element incorporation into minerals is now widely recognized. Its most accepted parameterization – the crystal lattice strain model – is increasingly being applied with success in experimental and empirical petrology. The fundamental premise of the crystal lattice strain model is that isovalent trace element incorporation is governed mainly by two factors, the radius of the substituent cation and the elastic modulus of the substituent lattice site.

This paper presents an empirical study that tests the premise of the crystal lattice strain model with a combination of high precision crystallographic and lanthanide data for the mineral clinopyroxene. Multiple aliquots of very small subgrains (ca. 50 μm diameter) were exposed to repeat XRD analysis (Gandolfi camera) and subsequently chemically analyzed by low-blank miniaturized solution ICP-MS procedure. Additional in situ chemical analyses were also obtained by laser ablation ICP-MS. Using Rietveld analysis, the XRD data define the structural parameters of the crystal, including the exact geometry of the M2 and M1 sites. The lanthanide data, when normalized to an appropriate bulk rock composition, yield a normalized concentration with similar effectiveness to the distribution coefficient. The apex of the resulting Onuma diagram is centered over the ideal radius, which can be quantified using a plot of radius parameter versus the natural logarithm of the apparent distribution coefficient. The combined dataset thus yields two completely independent estimates for the effective radius of the M2 cation (and for two samples also the M1 cation), for which the lanthanides substitute.

Comparison of the two independent estimates for the ideal radius yielded a robust positive correlation ($r^2 = 0.879$) with a slope of 0.911 for 4 of the 5 studied specimens and even stronger agreement, when M1 data are included. This study thus provides very strong empirical evidence that adds to a growing database of experiments showing the validity of the crystal lattice strain model.

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1. Introduction

The crystal lattice strain model (CLSM) successfully describes trace element distribution in many experimental and empirical geochemical datasets, including the rare-earth elements (REEs) in common rock-forming minerals such as clinopyroxene (cpx, e.g. Hill et al., 2000; Fedelle et al., 2000; Hill et al., 2011), plagioclase (e.g. Hattori and Sato, 1996; Bindeman et al., 1998), and garnet (e.g. van Westrenen et al., 1999, 2001; van Westrenen and Draper, 2007). Thus, the CLSM provides a convenient crystal-chemical rationalization for trace element distribution (Brice, 1975; Blundy and Wood, 1994; LaTourrette et al., 1995). At the very heart of the CLSM is the concept that the apparent polyhedral elastic modulus combined with the effective ionic radius of a host site

exerts control over the relative partition coefficients of isovalent cations that may occupy that site. Since the much-cited paper by Blundy and Wood (1994), the CLSM has gained very wide acceptance in the geochemical and petrological communities and a great number of trace element datasets have been successfully interpreted with this approach (e.g. Blundy and Dalton, 2000; Adam and Green, 2003; Lee et al., 2007).

In view of the wide acceptance of the CLSM and proliferation of its data for cpx, it is somewhat surprising that the fundamental crystallo-chemical premise of the model (i.e. constraint of isovalent atomic admittance to a specific lattice site based on atomic radii) has not yet been investigated for cpx. One of the few such tests was performed by Bottazzi et al. (1999), who successfully compared structural parameters obtained from single crystal X-ray diffraction (XRD) with chemical data for amphiboles collected using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Despite the structural and chemical complexity of amphibole, data from the Pavia group shows promising results. Owing to advances in XRD, specifically single crystal XRD and image plate technology, it is possible to calculate (via Rietveld refinement) both accurate and precise

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structural parameters (i.e. unit cell dimensions, fractional atomic coordinates and thermo-isotropic parameters) from crystals or crystal fragments of 25 μm diameter or smaller. These datasets can be compared with the normalized concentrations of element i ($NC = i$ concentration in mineral/ i concentration in presumed whole rock, discussed further below) for trace elements to test the fundamental assumptions behind the CLSM.

The objective of this study was to perform such a comparison for natural cpx, which was chosen because of its ability to incorporate the full range of REE and because the M2–O bond length minus the radius of O is typically between the largest (La 1.16 Å) and smallest (Lu 0.977 Å) REEs. In other words, the apex of an Onuma diagram for the M2 site of the cpx is within the range of observation, unlike in many other rock forming minerals. For example, in garnet the crystallographic site of REE substitution is smaller than Lu (X-site ≤ 0.97 Å) and in plagioclase it is larger than La (A-site ≥ 1.17 Å) as illustrated in Fig. 1. For these minerals, it is more difficult to constrain the size of the substitution site with adequate precision from REE information and therefore minerals with a lattice site larger or smaller than the observable REE may benefit greatly from this technique.

The structure of cpx is characterized by three crystallographically unique polyhedra coordinated by O. These are the 6-coordinated metal-site (M1), the 8-coordinated metal-site (M2), and the 4-coordinated tetrahedral or T-site. Rare-earth elements mainly occupy the eight coordinated M2 site, while the four coordinated T-site is too small to accommodate the REE. In low-alumina cpx, the heavy REEs (HREEs) have also been reported to substitute into the six coordinated M1 site (Fedele et al., 2000; Olin and Wolff, 2010; Hill et al., 2011). The main question behind this study thus was whether the chemical and crystallographic data for REE substitution were mutually consistent.

2. Materials and methods

Where possible, an effort was made to study high quality crystals. The represented occurrences fall into four groups: a gem quality diopside from a potassic alkaline ultramafic complex (Inagli Cr-diopside); a further gem quality diopside from a carbonatite (Deeti Al-diopside); one omphacitic clinopyroxene from an eclogite; and two Cr-diopsides (grains #39 and #56) from kimberlite heavy mineral concentrates interpreted to have been derived from refractory garnet peridotite. These specimens were chosen to provide a range in crystal chemistries and formed in distinctive geological environments.

Trace element data were produced in duplicate by two independent analytical techniques. In situ LA-ICP-MS was performed on

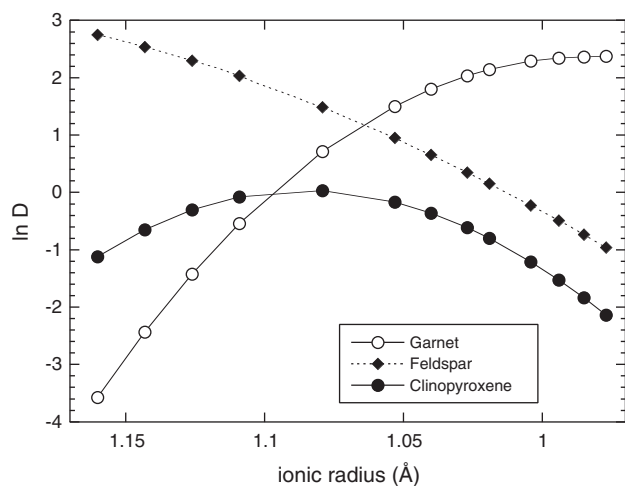


Fig. 1. Ideal Onuma REE diagrams for garnet, with an ideal radius smaller than Lu, plagioclase, with an ideal radius greater than La and clinopyroxene, with ideal substitution in the middle REE.

polished grain mounts and very small crystal fragments (ranging in mass from 1.60 to 0.133 mg) were analyzed by solution ICP-MS to minimize the risk of systematic calibration bias. The crystal structural parameters were obtained using a Gandolfi based 'powder' diffractometry technique (Petrus and Ross, 2011; Petrus et al., 2012).

2.1. Chemical analysis

2.1.1. In situ geochemical analysis

Major element data were obtained from carefully polished grain mounts and thin sections. The grains were analyzed by wavelength dispersive spectrometry on a Cameca SX-100 electron microprobe (EMP) at the Ontario Geological Survey Geolabs. The instrument was operated with an acceleration voltage of 20 kV and a beam current of 20 nA. One specimen (Deeti) was analyzed by energy DS (EDS). Well characterized natural and synthetic standards were used for calibration.

In situ trace element data were obtained by ultra violet (UV) LA-ICP-MS using a Supercell™ equipped NewWave™ Nd:YAG 213 nm laser coupled to a ThermoFisher™ X Series II quadrupole ICP-MS. Grain mounts and polished sections were ablated in 99.9995% pure He carrier gas (ca. 0.5 l min⁻¹), which was mixed immediately down-stream with Ar (0.8 l min⁻¹) to ensure efficient aerosol transfer to the plasma (e.g. Kamber, 2009). Where possible, a 100 μm spot size was used and the laser was fired with a repetition rate of 10 Hz. Fluence was kept constant at 11 J·cm⁻². The total analysis time was typically 70 s, consisting of 30 s background acquisition, 25 s of ablation, and the remainder being washout. The synthetic glass standard NIST612 was used for calibration with Ca (as determined from the electron microprobe analyses) as the internal standard (e.g. Heinrich et al., 2003). Data quantification was performed with the Iolite software (Hellstrom et al., 2008).

2.1.2. Solution ICP-MS data

A very small fragment (ranging from 1.6 to 0.133 mg) of each studied cpx was also analyzed for extended trace element compositions using solution ICP-MS; except for the Bakersville eclogite omphacite, where insufficient material remained after LA-ICP-MS and XRD analyses. Fragments were digested in 6 ml Teflon™ vials using a mixture of 0.4 and 0.1 ml double and triple, respectively, sub-boiling distilled HF and HNO₃ for 72 h at 160 °C on a hotplate. After conversion with HNO₃, the solutions were diluted with 6 ml of 2% HNO₃ and spiked with 4.4 ppb of ⁶Li, Rh, Re, Bi and ²³⁵U. Instrument response was calibrated with two independent digestions of USGS dolerite standard W-2 (Kamber, 2009). Even at the exceedingly low concentrations given from such small samples, this technique has produced REE data with internal errors and accuracy better than 4% (Babechuk et al., 2010).

2.2. Crystal structural data

2.2.1. Powder XRD

Powder X-ray diffraction data were obtained with a 114.59 mm Gandolfi camera, employing a Ni filtered CuK α radiation (average wavelength 1.1564) and operating conditions of 40 mA and 30 kV. The camera was equipped with a 0.3 mm pin-hole collimator and rotary vacuum pump capable of achieving an absolute pressure of 0.03 atm. The exposure times ranged between 4 and 10 h. For X-ray detection a BaFBr:Eu²⁺ FUJIFILM SR-type image plate (IP) was used. Individual grain fragments were gently crushed in an agate mortar then affixed to the end of a tapered glass fiber (100 drawn to 15 micron diameter) using fingernail hardener. The grain cluster had a total volume of $\approx 200 \mu\text{m}^3$ consisting of at least 20 grains. A sufficient number of differently oriented grains with respect to the incident X-ray beam reduced the likelihood of reflection absences caused by preferred orientation.

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