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A recipe for laboratory-grown crystals

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Abstract

Clinopyroxenes are among the first minerals to crystallize out of a ferromagnesian silicate magma. They commonly exhibit "sector zoning", a phenomenon whereby the crystal incorporates elements in different proportions on non-equivalent crystal faces. By growing clinopyroxene crystals in the laboratory, it is possible to investigate controls on compositional variation, which provides insight on magmatic processes. The goal of this research was to develop an experimental method for growing synthetic clinopyroxene (a silicate mineral) in a carbonate melt rather than in a silicate one. This is advantageous since silicate residue on the clinopyroxene crystal may damage crystal faces, which contain important information on growth features, unlike carbonate residue which is easily dissolved leaving crystal faces intact. The carbonate melt was modeled after the alkali-rich carbonatite lavas erupting at Oldoinyo Lengai, Tanzania by using powdered clinopyroxene, magnetite and alkali carbonates containing up to 5% wt. water as starting materials, and running the experiment at conditions of 800∞C and 10 kbars. Clinopyroxene crystals in a carbonate crystalline matrix were retrieved from the experiment capsules, and cleaned for imaging and analysis with the atomic force microscope (AFM), scanning electron microscope (SEM) and electron microprobe (EMP). This experimental approach provides well-preserved crystal faces whose surfaces can be examined at nanoscale resolution. This technique could be applied to a wide range of synthetic silicate minerals, and the resulting observations help to better understand the relationship between crystal surface structure and trace element uptake during crystal growth.

Keywords

Carbonate/silicate melt: *a synthetic liquid meant to mimic natural magma in which crystals grow; the melt can be silica-dominated (silicate melt) or carbonate-dominated (carbonate melt);* **clinopyroxene**: *a silicate mineral commonly found in nature with a composition of* $Ca(Mg,Fe)Si_2O_6$; **crystal lattice**: *3D geometric arrangement of atoms in a crystal;* **crystalline matrix**: *a fine-grained crystalline matter in which larger crystals are embedded;* **dislocation**: *a linear defect in the crystal structure which promotes growth;* **nucleation**: *the initial step in development of a crystal, where a sufficient number of ions must cluster together to overcome spontaneous separation of ions due to unstable configuration;* **sector zoning**: *phenomenon whereby different crystal faces unequally incorporate trace elements during crystal growth;* **weathering**: *processes by which rocks break down.*

Introduction

Clinopyroxenes are a mineral group described by the chemical formula $Ca(Mg,Fe)Si_2O_6$ and characterized by single chains of silica tetrahedra (SiO_4^{4+}), giving them a prismatic shape elongated along the direction of the c-axis **(Figure 1)**. They are abundant in nature and are one of the first minerals to crystallize from ferromagnesian (iron and magnesium-rich) silicate magma. Like most minerals, they incorporate small amounts of foreign ions during crystal growth, and their crystal chemistry offers insight into mantle and crustal processes (Skulski et al, 1994). A particular feature of clinopyroxene crystallization is the development of sector zoning, the unequal incorporation of trace elements (or "impurities") into the crystal lattice on different crystal faces. Natural and synthetic clinopyroxenes with sector-zoned trace (Sc, Ti, V, Cr, Mn, Co and Zr) and major (Mg, Al, Si, and Fe) elements have been described in the literature (Shimizu, 1981; Kouchi et al., 1983).

Although clinopyroxene crystals are commonly found in nature, it is advantageous to synthesize them in the laboratory for crystal chemical studies since the surfaces of naturally-occurring crystals are commonly damaged by physical and chemical weathering. Laboratory-grown crystals offer control over growth conditions; parameters are chosen to favor development of specific crystal features of interest. In this study, the preservation of intact crystal surfaces was prioritized. This enables observation of growth morphology on crystal faces, which may influence the development of sector zoning (Watson, 1996). Although the studies by Shimizu (1981) and Kouchi et al. (1983) analyzed impurities incorporated in natural and synthetic clinopyroxene crystals, they did not observe in detail the surface structure of freshly-grown crystal faces. The research presented here aims to develop a new and efficient experimental technique for growing clinopyroxene crystals that preserves the pristine crystal faces upon extraction from an encrusting crystalline matrix. Removing the freshly-grown crystals from their encrusting crystalline matrix without damaging the surface features developed during the experiment presents a significant challenge. The present study overcomes this problem by the use of a carbonate melt as the growth medium for clinopyroxene crystals, rather than the conventional silicate melt, since a carbonate matrix is easily dissolved in comparison to a more resistant silicate matrix. Undamaged experimentally grown crystals permit a thorough study of the influence of surface structure on sector zoning.

Methods

An alkali-rich carbonate lava erupted from Oldoinyo Lengai, Tanzania in 1993 (Dawson et al. 1994) was used as a model melt composition because clinopyroxene was reported as one of the minerals crystallized in the lava **(Table 1)**. The lava composition was replicated in the laboratory by using reagent-grade calcium carbonate ($CaCO_3$), magnesium

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*Corresponding author. E-mail: michelle@eps.mcgill.ca carbonate ($MgCO_3$), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and iron oxide (Fe_2O_3). For the source of silica, crushed natural clinopyroxene crystals from the Orford nickel mine in Québec, Canada **(Table 1)** were added to the reactant mixture rather than reagent-grade silica, since the presence of natural clinopyroxene in the melt encourages growth, even in its powder form. By using natural clinopyroxene powder, minor amounts of trace elements are added (Co, Cu, Zn, Sr, etc.), but these are insignificant to this study which focuses on sector zoning of the major elements (Ca, Mg, Fe, Al, Si). The powders were thoroughly mixed with ethanol for 30 minutes using a mortar and pestle, and left under a heating lamp overnight to dry. The reactant mixture was then placed in three 2 x 9 mm AuPd capsules to which were added 0, 2.5, and 5 wt% distilled H_2O respectively, with a microliter-scale syringe. The addition of water to the experimental capsules tests the ability of an anhydrous melt (0 wt% H_2O) in comparison to a hydrous melt (2.5 and 5 wt% H_2O) in generating growth. A risk presented by introducing H_2O to the melt is growth of a hydrous mineral rather than clinopyroxene, which is an anhydrous mineral. A 1 mm fragment of natural clinopyroxene, also from the Orford nickel mine, was added to each capsule to seed growth. The capsules were inserted into a piston-cylinder apparatus, which produces the high temperatures and pressures typical of the Earth's crust. The experiment ran for 24 hours at a temperature of 800˚C and a pressure of 10 kbar, approximately equivalent to a depth of 37 km below the Earth's surface, or the base of the crust, and subsequently quenched isobarically. Material recovered from the capsules was submerged overnight in dilute acetic acid, in the proportions four parts distilled water to one part acetic acid, to dissolve the carbonate matrix and retrieve the clinopyroxene crystals.

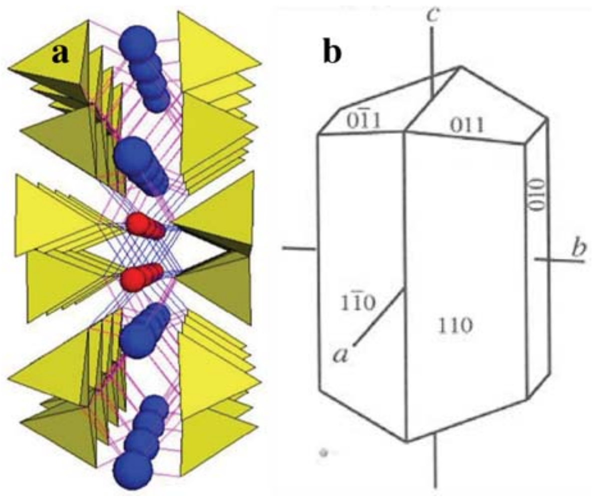

Figure 1. a) Chains forming the atomic structure of clinopyroxene. Yellow pyramids: tetrahedrally-bonded silica (SiO_4^{4-}). Blue spheres: Ca^{2+} cations. Red speheres: Mg^{2+} and Fe^{2+} cations. b) Dominant clinopyroxene crystal faces (110), (011) and (010) and crystal axes a, b and c. Chains of silica tetrahedra are oriented parallel to the c-axis, giving the crystal its elongate shape.

The AFM, SEM and the EMPwere used to identify the presence of crystal overgrowth on the natural clinopyroxene seed by observing growth morphology and analyzing chemical composition. The EMP cannot distinguish between atoms of different valence state, therefore the chemical analyses report all iron as ferrous iron (FeO). The amount of ferric iron (Fe_2O_3) present may be determined by performing a recalculation which satisfies charge balance. This recalculation uses an equation which assumes that iron is the only atom in the melt with variable valency, that oxygen is the only anion and that all cation sites in the mineral formula of clinopyroxene are full (Droop, 1987).

Results

The crystals retrieved ranged in size from 0.1 – 1.0 mm, and displayed a greenish hue typical of Fe-rich clinopyroxene, whereas the seed was 1mm in size and of a yellowish colour. Several analytical tests were performed on the retrieved crystals to identify the presence of crystal overgrowths, their mineralogy and chemical composition.

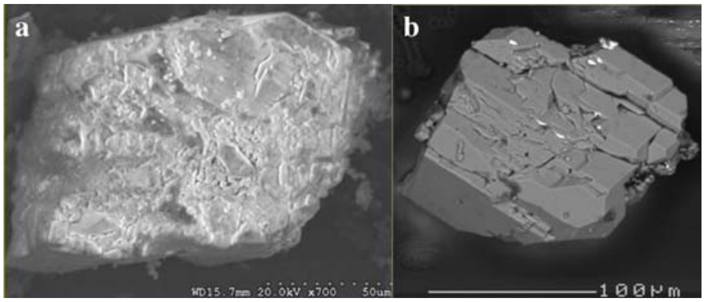

Figure 2. SEM images of clinopyroxene crystals. a) Before acetic acid wash: abundant carbonate residue covers the crystal surface. b) After acetic acid wash: the carbonate residue has dissolved, exposing well-defined crystal faces and edges.

Scanning Electron Microscope (SEM)

The SEM produces high resolution images with well-defined three-dimensional features by firing an electron beam at an area and recording the ensuing emission of electrons from the surface. A SEM images shows the general morphology of the crystal, and permits a preliminary identification of visible crystal faces, as depicted in **Figure 1b**. SEM imaging also reveals any matrix residue still encrusted on crystal surfaces. The crystal cleaning protocol may then be modified accordingly, as a longer soak or a stronger acid may be necessary to successfully dissolve all crystalline matrix. **Figures 2a** and **2b** are images taken with the SEM. **Figure 2a** shows a seed fragment after a 12-hour soak in distilled water. The crystal is still considerably encrusted with its crystalline matrix. Subsequently, the crystals were submerged in dilute

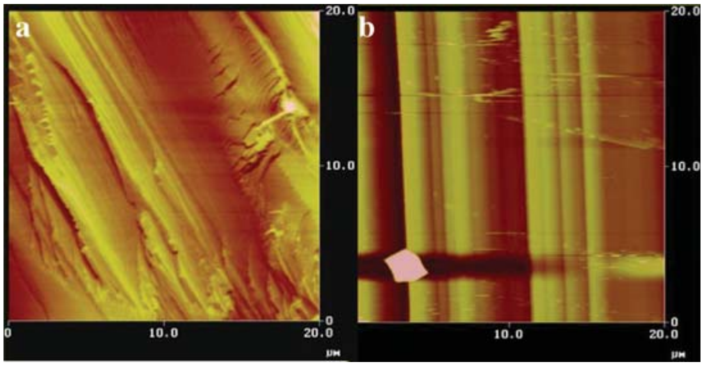

Figure 3. AFM images of synthetic crystal surface topography. a) Fractured surface. b) Parallel growth steps; cubic form at bottom left is likely an iron oxide crystal.

acetic acid for 12 hours which successfully dissolved the crystalline matrix, as shown by the clean crystal in **Figure 2b**. **Figure 2b** also reveals some well-developed crystal faces.

If the faces are large enough, the crystals may be mounted with such faces facing upwards for scanning with the atomic force microscope (AFM).

Atomic Force Microscope (AFM)

The AFM is an instrument equipped with a sharp tip mounted on a cantilever which scans the surface of crystals and detects surface topography down to the near-atomic scale. This tool thus enables visualization of growth structure, if present. Although this method permits the qualitative analysis of growth features, it cannot be determined whether the features observed belong to the natural seed fragment or were generated over the course of the experiment and indicate new growth. Imaging of the experimental crystals must therefore take into account the possibility that surface topography observed predates the experiment. Nonetheless, this analysis is a crucial step in thoroughly characterizing experimental results. **Figures 3a** and **3b** were taken with the AFM. The splintery texture and jagged edges observed in **Figure 3a** strongly suggest a freshly cleaved surface. In contrast, **Figure 3b** reveals parallel, elongate growth steps which either reflect fresh overgrowth from the experiment, or a growth surface present on the original clinopyroxene seed.

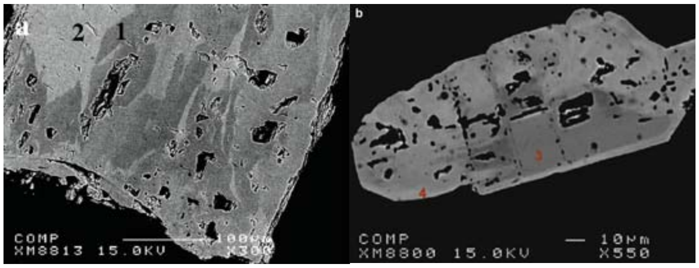

Figure 4. BSE EMP images of synthetized clinopyroxene crystals. Dark and light zones indicate areas of heavier and lighter average mass respectively. Black areas on the crystal surfaces are holes due to polishing. Chemical analyses for numbered areas are given in **Table 1**, with special care given to sampling both dark and light zones.

Electron Microprobe (EMP)

The EMP determines the chemical composition of a solid surface by bombarding the mineral surface with electrons and recording the energy of the emitted x-rays. Minerals and their composition may be identified, as each constituent element emits a characteristic reflected x-ray photon energy. The EMP is performed last in the series of analytical techniques since it requires a polished surface for probing, hence destroying all surface growth features. For this experiment, the reactant mixture departed significantly from the original Orford nickel mine clinopyroxene composition by the addition of alkalis (Na_2O, K_2O) and ferric iron (Fe_2O_3) to the melt. The seed, which was submitted for EMP chemical analysis, contained only trace amounts of Na_2O and K_2O, and mostly ferrous iron (FeO) **(Table 1)**. This contrast in composition between the seed and the melt facilitates monitoring of element exchange between the melt and growing crystal. **Figures 4a** and **4b** are images taken by back-scattered electron imaging with the EMP, and corresponding quantitative chemical analyses for the numbered spots are reported in **Table 1**. The lighter-shade zones numbered 2 and 4 reflect lighter average atomic mass. The darker-shade areas numbered 1 and 3 have heavier average atomic mass, as they have higher concentrations of FeO, CaO and MgO than the lighter areas, which in turn have higher concentrations of Na_2O, K_2O and Fe_2O_3. These lighter patches therefore indicate incorporation of melt elements into the crystal structure.

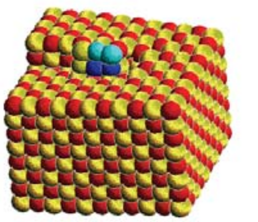

Figure 5. Dislocation–linear defect in the crystal lattice which promotes growth by creating nucleation sites.

Discussion

A 1mm natural clinopyroxene fragment was used to seed growth, yet several smaller crystals were retrieved from each capsule after the experiment. This suggests that the 1mm seed fragmented into several smaller pieces during the experiment, onto which growth may or may not have occurred. Another possible explanation is that the seed was partially to completely dissolved over the course of the experiment, and nucleation gave rise to several small crystals. The latter possibility is unlikely, as nucleation is a difficult process to initiate and requires a considerable amount of energy. If the first explanation is accepted, the fragmented seed could considerably enhance chances of new growth by increasing available crystal surface area.

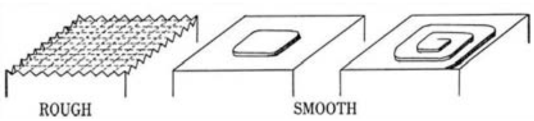

Figure 6. The stages of dislocation-controlled growth: initially rough surface, formation of a growth hillock and growth layers around the hillock.

The initial appearance of the retrieved crystals suggests the experiment was successful in generating element exchange between the melt and seed: the synthetic crystals were a darker shade of green than the seed, which was closer to yellow. Darker coloring indicates higher iron content; as the melt was enriched in ferric iron, the fragmented seed likely incorporated iron from the surrounding melt. This greenish hue may only signify re-equilibration of the crystal with its growing medium, and not necessarily the occurrence of new growth layers. Further evidence for growth is provided by AFM and EMP analyses.

	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Cr2O3	Total
1	54.00	-	0.26	0.94	4.11	0.22	15.16	25.48	0.05	0.01	0.01	100.24
2	54.00	0.02	0.24	8.90	-	0.08	13.93	19.89	3.19	0.01	0.04	100.3
3	53.44	-	0.39	0.86	5.45	0.21	14.33	25.16	0.08	-	-	99.92
4	52.48	-	0.80	17.63	-	0.01	7.69	11.41	7.43	0.13	0.13	97.71
Seed (Orford nickel mind)	53.28	-	0.73	1.12	4.87	0.35	14.26	25.18	0.17	-	-	99.96
1993 lava	3.12	0.12	1.02	1.49	-	0.37	0.30	15.93	29.09	5.87	-	-

Table 1. EMP spot chemical analyses corresponding to numbered areas on crystals in **Figure 4** and of the original Orford clinopyroxene used as a seed in the experiments. Composition of the model 1993 lava from Oldoinyo Lengai. Values are reported in weight %.

Imaging with the AFM revealed the presence of parallel growth steps, a feature associated with dislocation-controlled growth. Dislocations result in the formation of a ramp on an otherwise flat surface **(Figure 5)**. This ramp encourages growth as nucleation sites are created along the leading edge of the ramp. Initial stages of growth resemble hillocks (**Figure 6**). The structure then follows a helical path around the hillock, continuously adding growth layers. On a smaller scale, these resemble steps, as those observed in **Figure 3b**. The parallel steps strongly suggest a freshly-grown surface. As discussed previously, the possibility exists that growth steps were present on the original seed before the experiment. Conversely, the parallel steps are not likely due to growth on the seed predating the experiment since the seed was heavily fragmented during the experiment; consequently, we would expect fractured surfaces as in **Figure 2a** rather than growth surfaces. Further evidence from the EMP chemical analyses is necessary to conclude the presence of new growth.

The EMP images and chemical analyses offer many possible interpretations. At first glance, **Figure 4a** and especially **Figure 4b** have darker-colored patches at the center of the imaged crystal. From **Table 1**, the numbered spots 1 and 3 in these darker areas have a composition very close to that of the seed. This observation leads to the interpretation that the central dark area is seed material, surrounded by a significant lighter-colored rim of overgrowth, which is high in melt constituents Na_2O, K_2O and Fe_2O_3. Another possible interpretation is that both dark and light areas represent new growth, and the uneven distribution of elements is the manifestation of sector zoning. Accordingly, the dark areas are enriched in Ca^{2+}, Mg^{2}+ and Fe^{2}+, and the light areas in Na^{+}, K^{+} and Fe^{3+}. In sector zoning, charge balance must be maintained, and coupled substitution of ions satisfies this condition. In this case, the coupled substitution reaction could be expressed as $(Ca^{2+}, Mg^{2+}) + Fe^{2}+$ ‡ $(Na^{+}, K^{+}) + Fe^{3+}$. This clarifies why the light domains are enriched in Na^{+} (Na_2O) but depleted in Fe^{2+} (FeO): the incorporation of Na^{+} into the crystal lattice is paired with Fe^{3+} to maintain charge balance. A third interpretation is that no new growth occurred. Although the dark centers with light rims are highly suggestive of overgrowth, the Fe_2O_3 and Na_2O enriched rims could simply reflect the re-equilibration of the seed fragment with the surrounding melt of differing composition by diffusion of ions through the crystal lattice until equilibrium is achieved. However, this third possibility is quite unlikely, due to the compelling evidence from the AFM images that growth steps are present on several crystal surfaces.

Conclusion

The major innovation of this research project was the choice of a carbonate melt as a growth medium for crystallizing a silicate mineral, clinopyroxene. Although clinopyroxene has been the subject of numerous crystal chemical studies, none have attempted this technique. The reference to a modern carbonate analogue, the Tanzanian volcano Oldoinyo Lengai, thus proves useful in modeling the experiment. The importance of developing an effective method for clinopyroxene crystallization lies in their common incorporation of trace elements from their surrounding magma. A better understanding of the mechanisms influencing this trace element uptake may lead to considerable advances regarding mantle and crustal studies. One such mechanism is the surface morphology of a growing crystal face, which may cause preferential elemental enrichment. To explore this concept, detailed observations of freshly grown crystal faces are imperative. The carbonate melt offers the advantage of an easily dissolvable crystalline matrix, from which clinopyroxene crystals may be freed while conserving undamaged surfaces. The results presented here confirm the efficacy of this technique, as the AFM imaged remarkably well-preserved growth steps, and the EMP confirmed the ability of a silicate mineral to incorporate elements from its carbonate environment. The method could therefore potentially be extended to a wide range of silicate minerals whose surface features one wishes to investigate.

The unconventional use of a carbonate melt as a growth medium for a silicate mineral does present potential limitations in applicability. Little information on the diffusivity of carbonate melts is available in the scientific literature, which makes a comparison with silicate melt diffusivity impossible. The diffusivity of the melt can play a major role in facilitating the migration of ions towards growth surfaces, and subsequently, may influence the ability of a crystal to incorporate trace elements. Carbonate magmas represent only a small fraction of all magmas on Earth, the majority being silicate in composition. The experiment would need to be replicated using a silicate melt to assess the degree of compositional and/or morphological difference in the results, but such a study is made difficult by the resistant encrusting matrix formed by silicates which destroys morphological features. Silicate environments also require higher running temperatures, which makes the experiments technically riskier to perform. A thorough comparative study of carbonate and silicate melt characteristics must be undertaken to justly assess the applicability of the experimental results presented in this study.

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