# Clinohypersthene and hypersthene from a coal fire buchite near Ravensworth, N.S.W., Australia

BASTIAAN J. HENSEN AND DAVID R. GRAY[1]

*School of Applied Geology, University of New South Wales*
*Kensington, N.S.W. 2033, Australia*

## Abstract

Clinohypersthene, $Fe_{1.02}Mg_{0.88}Ca_{0.04}Al_{0.05}(Si_{1.93}Al_{0.06})O_6$, space group $P2_1/c$, and hypersthene occur in two separate, partly glassy rocks a few feet apart in a buchite "chimney" associated with a burned coal seam. The clinohypersthene occurs as phenocrysts and is accompanied by plagioclase ($An_{80}$), cordierite [$Mg/(Mg + Fe^{2+}) = 0.65$], spinel ($Mt_{52}Uv_{26}Hc_{22}$), and brown glass. The hypersthene has the same Wo content but is more magnesian [$Mg/(Mg + Fe^{2+}) = 0.50-0.52$] than the nearby clinohypersthene [$Mg/(Mg + Fe^{2+}) = 0.30-0.46$]. The data suggest that the two-phase region marking the ortho-pyroxene-to-pigeonite transition in the system $CaO-MgO-FeO-SiO_2$ intersects the enstatite-ferrosilite join. The clinohypersthene probably crystallized at a temperature above $1060°C$.

## Introduction

As far as we are aware, clinohypersthene (space group $P2_1/c$) has not been previously reported occurring as discrete crystals in terrestrial rocks. Clinohypersthene lamellae (0.5–0.7 percent CaO) in augite have been described from metamorphic rocks (Binns, 1965) and from slowly-cooled igneous rocks (Binns *et al.*, 1963). In the present occurrence the clinohypersthene has crystallized directly from a liquid and is thus clearly of a different origin. This occurrence of clinohypersthene is of particular interest because closely adjacent rocks contain orthopyroxene with the same wollastonite content ($Wo_2$), but with a slightly higher enstatite content. This suggests that the $Mg/(Mg + Fe^{2+})$ ratio is a major factor determining pyroxene stability. The data provide new information pertaining to the still poorly-understood phase relations involving Ca-poor pyroxenes at high temperatures, first studied by Bowen and Schairer (1935).

## Occurrence

The buchites occur near Ravensworth, N.S.W., Australia on portions 150 and 226, Parish Lidell, County Durham. The field aspect and mineralogy of

the rocks have been described by Whitworth (1958), who noted the presence of a "pale green feebly pleochroic pyroxene" of prismatic habit, atypical for basalt but of a type "often developed in furnace slags." The buchites and associated indurated sedimentary rocks occur as isolated roughly circular outcrops up to 15 meters in diameter, and may represent the surface expression of "chimneys" overlying a burned-out coal seam (Whitworth, 1958). The coal seam does not outcrop in the area studied. Slags similar to the ones described here occur immediately overlying cindered seams at Wingen, 45 km north of Ravensworth (David, 1907). Overburden of the seams was probably small, and sufficient air was available for combustion. Temperatures of 1200°–1400°C may have been reached, depending on the availability of oxygen. A more detailed description of the Ravensworth occurrence will be given elsewhere (Gray *et al.*, in preparation). A variety of fused and partially-fused rocks ranging from shale to sandstone occur, with a mildly to strongly vesiculated slag-like appearance. A dark-colored basic "slag," apparently less viscous than the more siliceous fused arenites, is usually seen to intrude the latter in the form of thin veins of mm to cm width. The rocks described in this paper were collected from a circular patch (approximately 1 m in diameter) of slag-like buchite surrounded by indurated red arenite. The buchite has a sharp irregular contact with the arenite and is miner-

alogically and texturally heterogeneous. The clinohypersthene-bearing sample was found immediately adjacent to the orthopyroxene sample within the buchite.

## Petrographic description

### Clinohypersthene-bearing vein

The clinopyroxene occurs in a thin black vein (0.2 cm wide) which intrudes a glass-rich vesiculated psammite containing relict quartz grains. The veins are locally vesiculated and contain a brown to nearly colorless glass (15–20 percent), clinohypersthene (*ca.* 30 percent), plagioclase (*ca.* 30 percent), cordierite (5–10 percent) and opaque spinel (5–10 percent). The texture is aphanitic, subophitic, with subhedral clinopyroxene phenocrysts, slender plagioclase laths with random orientation, small euhedral cordierite crystals, opaque spinel, and interstitial brown glass, locally containing pyroxene microlites. Cordierite and especially spinel tend to occur in grain clusters, and the volume percentage made up by these minerals varies within the vein. Plagioclase, cordierite, and spinel are sometimes wholly or partly enclosed by clinohypersthene. A fine-grained border zone, up to 0.4 mm wide, is found against the fused arenite. In this zone clinohypersthene is rare, and tridymite and mullite are common.

Clinohypersthene crystals show a pale green to pale brown pleochroism, have a subhedral prismatic habit, and are up to 0.5 mm wide and 1.5 mm long. Twinning is absent. The optical and X-ray properties are given in Table 1. The space group was determined as $P2_1/c$. Plagioclase occurs as thin tabular crystals,

up to 0.04 mm in thickness, displaying two to three albite twins. The extinction angle is large (up to 45°) indicating a very high anorthite content ($An_{80}$ by microprobe analysis, Table 2). Cordierite forms small euhedral stubby crystals with hexagonal end sections (up to 0.1 mm wide and 0.3 mm long). Hexagonal sections show a patchy extinction pattern rather than sector twinning. Opaque spinel occurs as equant and platy grains (0.1 mm diameter) often in clusters. It is mostly included in glass but is also found as inclusions in clinopyroxene. The glass is mostly brown in color. Local discoloration is rarely observed near pyroxene crystals.

The fused arenite surrounding the clinohypersthene-bearing vein consists of pink to colorless glass containing abundant small (0.01 mm) cordierite crystals with short hexagonal prismatic habit and rare orthopyroxene (?) microlites. Optical and X-ray determinations indicate that tridymite is common and cristobalite is relatively rare. Relict quartz grains are commonly rimmed with a thin rind of cristobalite.

### Orthopyroxene-bearing buchite

The orthopyroxene occurs in a fused arenite similar to the host rock of the clinohypersthene vein. The rock is strongly vesiculated and contains relict quartz grains. Aggregates of tridymite showing wedge-shaped twins occur together with pink glass, which also contains slender prismatic colorless orthopyroxene (0.04 mm wide, 0.8 mm long), cordierite, and rare plagioclase. The glass is nearly colorless in a 0.02 mm wide zone surrounding the orthopyroxene crystals. The presence of cristobalite as well as tridymite was confirmed by X-ray diffraction.

## Chemistry

Clinopyroxene and coexisting cordierite, plagioclase, spinel, and glass from the vein material, and orthopyroxene from the buchite, have been analyzed by electron microprobe (Table 2). The compositional variation of the pyroxenes in the two rocks is shown in Figure 1. The spread in $Mg/(Mg + Fe^{2+})$ values for the clinopyroxene is greater than was expected on the basis of optical observations, as the pyroxenes show no clear indications of zoning. The range of $Mg/(Mg + Fe^{2+})$ ratios is similar to that in phenocrysts of orthopyroxene and pigeonite in the Mull andesite, which has been attributed to fractionation (Virgo and Ross, 1973). The compositional variation of the orthopyroxene is relatively small, especially considering the inhomogeneous nature of the host rock.

Table 1. Optical and X-ray properties of clinohypersthene

| | | |
|---|---|---|
| $1.75 < \gamma <$ | $1.76$ | $2V_z = 0 - 5°$ |
| $\gamma - \alpha =$ | $0.026-0.027$ | $Z \wedge c = 44 - 46°$ |

pleochroism: $\gamma$ light green; $\alpha$, $\beta$, light yellow brown

| | | | |
|---|---|---|---|
| a | 9.72 | (1)* Å | |
| b | 9.06 | (1) Å | |
| | | | space group $\underline{P2_1/c}$ |
| c | 5.26 | (1) Å | |
| $\beta$ | 108.6° | | |

* Figure in parentheses is the estimated standard deviation for the last decimal place of the value to their left. The cell edges were determined by the Weissenberg and precession methods.

Table 2. Electron microprobe analyses* of mineral phases

| Phase | Sample L21 Clinohypersthene | | Glass | Sample L25 Hypersthene | |
|---|---|---|---|---|---|
| $SiO_2$ | 49.42 | 45.54 | 69.2 | 51.98 | 50.33 |
| $TiO_2$ | 0.12 | 0.28 | 0.58 | 0.91 | 0.73 |
| $Al_2O_3$ | 2.45 | 2.94 | 12.6 | 3.31 | 1.85 |
| FeO | 31.35 | 40.45 | 8.30 | 26.23 | 29.70 |
| MnO | 0.52 | 0.69 | 0.28 | 0.34 | 0.30 |
| MgO | 15.03 | 9.37 | 0.60 | 15.46 | 16.39 |
| CaO | 0.93 | 0.73 | 1.38 | 0.81 | 0.53 |
| $Na_2O$ | – | – | 1.11 | – | – |
| $K_2O$ | – | – | 6.02 | – | – |
| Total | 99.82 | 100.02 | 100.07 | 99.04 | 99.83 |
| Atomic proportions for 6 oxygens | | | | | |
| Si | 1.93 | 1.87 | | 1.98 | 1.95 |
| Ti | 0.004 | 0.010 | | 0.03 | 0.02 |
| Al | 0.11 | 0.14 | | 0.15 | 0.08 |
| Fe | 1.02 | 1.39 | | 0.84 | 0.96 |
| Mn | 0.02 | 0.02 | | 0.01 | 0.01 |
| Mg | 0.88 | 0.58 | | 0.88 | 0.94 |
| Ca | 0.04 | 0.03 | | 0.03 | 0.02 |
| Total | 4.00 | 4.04 | | 3.92 | 3.98 |
| $Mg/(Mg + Fe^{2+})$ | 0.46 | 0.29 | | 0.51 | 0.50 |
| Percent Wo | 2.0 | 1.6 | | 1.9 | 1.1 |

Phases coexisting with clinohypersthene are cordierite [$Mg/(Mg + Fe^{2+})$ = 0.65], spinel (52.3% magnetite, 26.1% ulvospinel, 21.6% hercynite) and plagioclase ($An_{80}$). Compositions by microprobe analysis.
* Analyses by T.P.D. probe at A.N.U. using the method of Reed and Ware, 1975.

Two points are worth noting in Figure 1. Firstly, the wollastonite content (*i.e.* $Wo_2$) of the ortho- and clinopyroxenes is about the same, and secondly there is a clear compositional gap between ortho- and clinopyroxenes with respect to their $Mg/(Mg + Fe^{2+})$ ratio at 0.46–0.50, with the orthopyroxenes on the Mg-rich side of the diagram. Both the clinopyroxene and the orthopyroxene have relatively high $Al_2O_3$ (2–3 weight percent $Al_2O_3$), reflecting formation at high temperature in an Al-rich environment. The Mull orthopyroxene ($Wo_2$) and pigeonite ($Wo_4$) contain up to 1.56 and 0.65 weight percent $Al_2O_3$ respectively (Virgo and Ross, 1973). The composition of the titanomagnetite spinel coexisting with clinohypersthene also reflects an Al-rich environment in having an abnormally high hercynite content (Table 1).

The very high Ca content of the plagioclase ($An_{80}$) and the intermediate to high Fe content of the clinohypersthene [$Mg/(Mg + Fe^{2+})$ = 0.30–0.46] indicate a very unusual liquid composition, reflecting an Al-, Ca-, Fe- and Si-rich and K- and Na-poor source material. This is also shown by the composition of residual brown glass (Table 2).

## Discussion

The glassy rocks containing the contrasting pyroxenes have resulted from the melting of sedimentary rocks of different compositions. The liquids were rich in gas bubbles, now in the form of vesicles. The liquids cooled quickly, giving rise to glassy rocks often exhibiting quench textures. Whitworth (1958) describes plumose and dendritic sheaf-like pyroxene and spinel aggregates, and hollow skeletal feldspars and cordierite crystals from the siliceous buchites. These typical quench textures are poorly developed in the rocks described here.

The chemical compositions of clinohypersthene and hypersthene are consistent with crystallization at essentially the same temperature from liquids with slightly different chemistry. Note that the coexisting

mineral phases are the same in both cases with the exception of opaque minerals, which are absent in the hypersthene-bearing domains in the buchite. Comparison with the Mull and Weiselberg pyroxenes (Fig. 1) shows that in the case of *coexisting* ortho- and clinopyroxene, the clinopyroxene is significantly more Ca-rich than the orthopyroxene. The similarity in Wo content of the pyroxenes in this case may be due to different parent bulk-liquid compositions.

The origin of the discrete clinohypersthene crystals clearly involves high-temperature growth from a liquid. Recent high-temperature single-crystal X-ray studies indicate high clinopyroxene (space group $C2/c$) is stable at liquidus temperatures, and inverts in the solid state to low clinopyroxene (pigeonite, space group $P2_1/c$) at a temperature around 725°C (Smyth, 1969, 1974). The clinohypersthene lamellae in augite described by Binns (1965) and Binns *et al.* (1963) formed at low temperatures, possibly under the influence of a shear stress (*cf.* Coe and Kirby, 1975; Robin, 1977). The ortho- and clinopyroxenes described here have probably crystallized at the same temperature, as suggested by their close proximity in the field and by the compositional gap between the two groups of analyses (Fig. 1). Application of the experimental data of Bowen and Schairer (1935) or the more recent work of Ross *et al.* (1973) is wrought with some difficulty, as will be shown below.

The natural occurrence of a high-temperature very Ca-poor clinopyroxene gives support to the assumption that the two-phase field representing the orthopyroxene to high clinopyroxene transition in the system $MgO-FeO-CaO-SiO_2$ intersects the En–Fs join, as suggested by experimental studies (Hensen, 1973; Mori, 1978) and by X-ray investigations (Smyth, 1974). The geometry of the phase diagrams suggested by Huebner and Ross (1972, 1973), Hensen (1973),
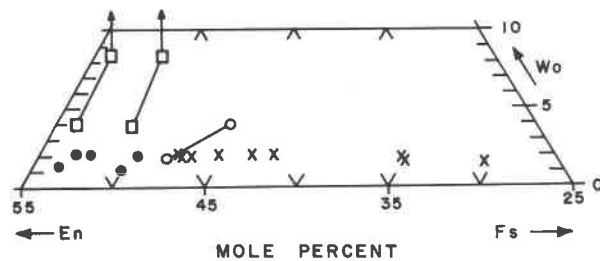


Fig. 2. Schematic phase relations in the pyroxene quadrilateral at high constant temperature. The $Mg/(Mg + Fe^{2+})$ ratio of coexisting orthopyroxene and pigeonite varies considerably as a function of their Wo content at constant temperature, as shown by tie-lines. The three-phase triangle clinopyroxene–orthopyroxene–pigeonite moves to the left with increasing temperature.

and Mori (1978) indicate that the Wo content of coexisting pyroxenes strongly influences their stability (Fig. 2). As a result, the attempt to use the $Mg/(Mg + Fe^{2+})$ ratio of pyroxenes in the transition as a geothermometer should be approached with care, as this ratio can vary considerably as a function of the Wo content at constant temperatures (see Fig. 2). Thus the inversion curves of Bowen and Schairer (1935) and Ross *et al.* (1973), determined with natural pyroxenes with a range of Wo contents, may need revision to take into account the effect of Ca on the equilibrium. In addition, the present pyroxenes contain up to 3 weight percent $Al_2O_3$, which may have a significant effect on the transition temperature. Taking these uncertainties into account, a crystallization temperature of above 1060°C can be derived from the data of Ross and Huebner (1975). This temperature range is consistent with the formation of liquid at low pressure, and with the occurrence of tridymite and mullite.

Fig. 1. Composition of clinohypersthenes (crosses) and orthopyroxenes (full circles) from Ravensworth, N.S.W. Open squares and open circles represent coexisting orthopyroxenes and pigeonites from the Weiselberg and Mull andesites respectively [data from Nakamura and Kushiro (1970) and Virgo and Ross (1973)]. The upward arrows indicate coexisting augite.
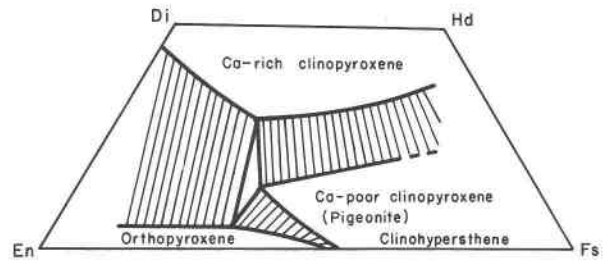
## References

Binns, R. A. (1965) The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, N.S.W. Part II. Pyroxenes, garnets, plagioclases, and opaque oxides. *Mineral. Mag., 35,* 561–587.
———, J. V. P. Long and S. J. B. Reed (1963) Some naturally occuring members of the clinoenstatite–clinoferrosilite mineral series. *Nature, 198,* 777–778.
Bowen, N. L. and J. F. Schairer (1935) The system MgO–FeO– $SiO_2$. *Am. J. Sci., 29,* 151–217.

Coe, R. S. and S. H. Kirby (1975) The orthoenstatite to clinoenstatite transformation by shearing and reversion by annealing: mechanism and potential applications. *Contrib. Mineral. Petrol., 52*, 29–55.

David, T. W. E. (1907) *Geology of the Hunter River Coal Measures of N.S.W.* Mem. Geol. Surv. N.S.W. No. 4.

Hensen, B. J. (1973) Pyroxenes and garnets as geothermometers and barometers. *Carnegie Inst. Wash. Year Book, 72*, 534.

Huebner, J. S. and M. Ross (1972) Phase relations of lunar and terrestrial pyroxenes at one atmosphere. *Lunar Science, 3*, 410–412.

—— and —— (1973) Partial melting of pyroxenes and the origin of mare basalts. *Lunar Science, 4*, 397–399.

Mori, T. (1978) Experimental study on pyroxene equilibria in the system $CaO-MgO-FeO-SiO_2$. *J. Petrol., 19*, 45–65.

Nakamura, Y. and I. Kushiro (1970) Equilibrium relations of hypersthene, pigeonite andesite from Weiselberg, Germany. *Am. Mineral., 55*, 1999–2015.

Reed, S. J. B. and N. G. Ware (1975) Quantitative electron microprobe analysis of silicates using energy-dispersive X-ray spectrometry. *J. Petrol., 16*, 499–519.

Robin, P. Y. F. (1977) Shear induced phase transitions in multi

component minerals (abstr.). *Trans. Am. Geophys. Union, 58*, 506.

Ross, M. and J. S. Huebner (1975) A pyroxene geothermometer based on composition–temperature relationships of naturally occuring orthopyroxene pigeonite and augite (abstr.). Int. Conf. on Geothermometry and Geobarometry, The Pennsylvania State University, University Park, Pennsylvania.

——, —— and N. Hickling (1973) Delineation of orthopyroxene–pigeonite transition and its bearing on pyroxene phase relations in lunar rocks. *Lunar Science, 3*, 637–639.

Smyth, J. R. (1969) Orthopyroxene–high-low clinopyroxene inversions. *Earth Planet. Sci. Lett., 6*, 406–407.

—— (1974) The high temperature crystal chemistry of clinohypersthene. *Am. Mineral., 59*, 1069–1082.

Virgo, D. and M. Ross (1973) Pyroxenes from Mull andesites. *Carnegie Inst. Wash. Year Book, 72*, 535–540.

Whitworth, H. F. (1958) The occurrence of some fused sedimentary rocks at Ravensworth, N.S.W. *J. R. Soc. N.S.W., 92*, 204–208.