

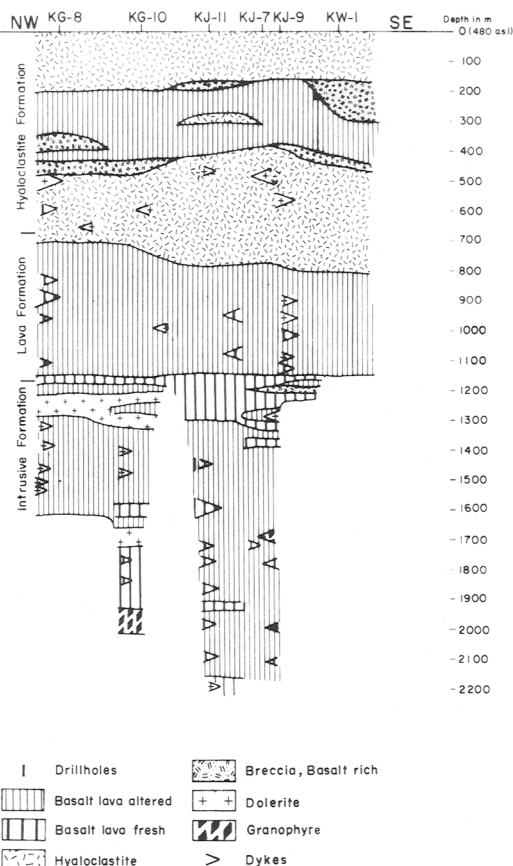
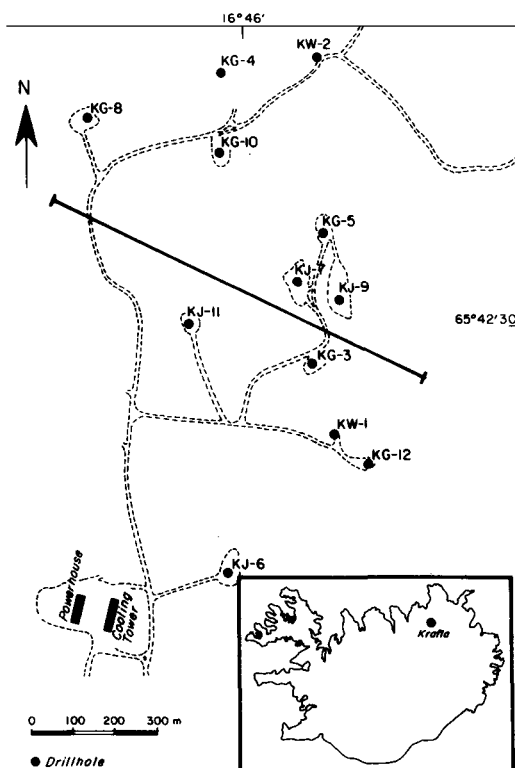
Wollastonite from hydrothermally altered basaltic rocks in Iceland

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ABSTRACT. Wollastonite is reported, for the first time in Iceland, in hydrothermally altered basaltic rocks in the Krafla high-temperature geothermal area, northern Iceland. Two possible modes of origin are suggested: (1) A contact metamorphic origin at the expense of hydrothermal quartz and calcite near the margins of dykes. (2) A hydrothermal origin at depths below 1000 m where fluid temperatures exceed 300 °C.

THE Krafla geothermal area (fig. 1) is within a caldera collapse of an active central volcano. The area has been active tectonically for the last five years (Björnsson *et al.*, 1979), and four volcanic eruptions have occurred during this time. In historical time one similar major volcanic and tectonic event is recorded.



FIGS. 1 and 2. FIG. 1 (left). Location of the Krafla geothermal area and the NW-SE stratigraphic section shown in fig. 2. FIG. 2 (right). Stratigraphical section through the Krafla geothermal area. Horizontal scale same as vertical scale. Location of the section is shown in fig. 1.

Twelve deep drillholes (1150–2200 m) have been drilled into the geothermal area in the years 1974–8, showing that intrusive activity has been intensive in the area. The holes penetrate tholeiitic basalt lavas and hyaloclastite ridge formations in the uppermost 800–900 m (fig. 2). Below this, basalt lavas are predominant. Dykes are common. The frequency of intrusive rocks increases with depth, and below 1000–1500 m they are predominant. The rocks are heavily altered by hydrothermal solutions. A regional alteration zoning is found with increasing temperature and depth (see Kristmannsdóttir, 1979).

The maximum temperature measured in the drillholes just exceeds 340 °C at 2000-m depth, but even higher reservoir temperatures are inferred. In zones of low permeability the rock temperature is close to the boiling-point of water at the corresponding pressure. The geothermal fluid at depth is neutral to slightly alkaline, with a high CO₂ content (Table I). During the recent volcanic activity the CO₂ content has increased greatly, probably due to volatilization from magma. An abrupt drop in pH for a short duration has also been observed in the discharge from a drillhole in the area.

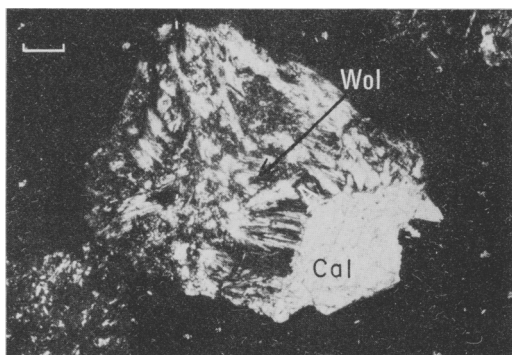


FIG. 3. Wollastonite (Wol) growing at the expense of calcite (Cal). Scale bar = 0.1 mm.

Occurrence of the wollastonite. The wollastonite forms aggregates of small fibrous crystals. A genetic relationship to calcite or quartz is often observed (fig. 3). Quartz or calcite vein fillings are commonly partly converted to wollastonite. Epidote and wollastonite are also often associated and are rather common vein fillings in the intrusive dominant zone below 1000–1500 m depth. The prevailing rock temperature at the shallowest depth where wollastonite occurs (600 m) is about 200 °C. At that depth the wollastonite is confined to narrow zones and is not found scattered between them. The wollastonite is here almost exclusively found

in the neighbourhood of dykes. In a few of the contact-metamorphosed vein fillings andradite garnet, hypersthene, and magnetite are found together with the wollastonite.

The wollastonite occurs more frequently with increasing rock temperature and depth. At greater depths (below 1000 m and at temperature 300 °C) a relation between the occurrence of wollastonite and intrusives is not always clear. However, as pointed out previously the frequency of intrusives increases strongly with depth. Calcite does not precipitate from the hydrothermal fluid at temperatures exceeding 300 °C (below about 1000 m). Below that depth the wollastonite is associated with quartz and epidote and its formation from hydrothermal vein fillings is nowhere clearly demonstrated.

Mineralogical characteristics. The aggregates of wollastonite are all fine-grained and a single-crystal analysis was therefore not possible. Powder samples were run on a Guinier de Wolf camera showing a normal diffraction pattern of wollastonite. Some of the first X-ray runs indicated the presence of the monoclinic parawollastonite form. Later analyses of purified samples did not confirm this. Possibly both forms might be present locally, but the samples chosen for runs on the Guinier de Wolf camera proved to be wollastonite.

The infra-red absorption spectrum of the wollastonite (fig. 4) identifies it as a β -wollastonite (see Lazarev, 1972). Several chemical analyses were run

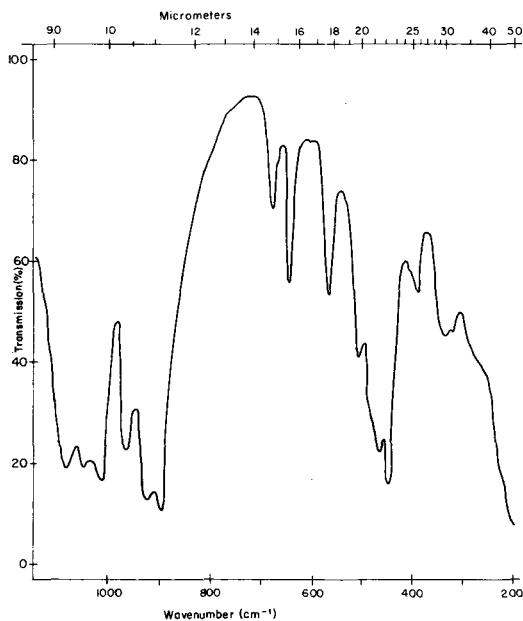


FIG. 4. The infra-red spectrum (far-infra-red part) of wollastonite from 830-m depth in drillhole KJ-11.

of the wollastonite on the microprobe, showing the composition to be fairly pure CaSiO_3 .

Origin of the wollastonite. For the wollastonite formed in the upper 1000 m in the Krafla area there is strong lithological and textural evidence for a contact metamorphic origin. A hydrothermal formation of wollastonite from calcite and silica at the prevailing temperatures down to 1000-m depth (200–240 °C) seems unlikely. From experimental studies of the reaction:



(Harker and Tuttle, 1956; Greenwood, 1967; Thompson, 1971) the minimum temperature of formation of wollastonite is inferred to be about 400 °C at $X_{\text{CO}_2} = 0$ and 1 kb total pressure. The formation temperature rises rapidly with increased mole fraction of CO_2 .

Hydrothermal minerals are commonly found to be formed in nature at lower temperatures than suggested by experimentally determined mineral equilibria (see Browne, 1977). Considering the experimental data, a hydrothermal formation of wollastonite at about 350 °C would thus not be surprising, whereas a formation temperature far below 300 °C is considered improbable. A contact metamorphic origin for the wollastonite in the upper part of the section, where the temperature of the geothermal system is below 300 °C, is therefore more likely. This is supported by the active volcanism in the Krafla area and its observed effects on the composition of the geothermal fluids.

The mole fraction of CO_2 in the totally vaporized hydrothermal fluid would be about 8.10^{-5} – 4.10^{-4} (Table I and unpublished NEA data).

TABLE I. *The composition of deep water (in ppm) from drillholes in the Krafla geothermal area*

	1	2	3
pH/°C	6.96/206*	6.74/224.9*	7.12/303*
SiO_2	300	374	681
Na^+	151	152	143
K^+	11.8	19.3	20.2
Ca^{2+}	2.1	2.6	1.1
Mg^{2+}	0.03	0.01	0.02
SO_4^{2-}	157.4	177.5	73.1
Cl^-	23.7	26.8	11.8
F^-	0.46	0.00	0.46
H_2S tot	63.4	14.8	92.4
CO_2 tot	271.7	543.2	10013

NEA data.

* Silica temperature.

The compositions are calculated from analyses of collected water and gases, assuming inflow from one aquifer.

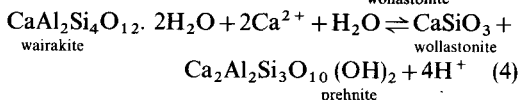
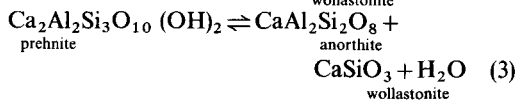
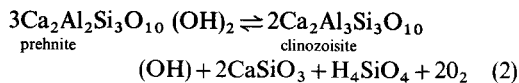
Volatilization from the magma would change this relation. The X_{CO_2} in the discharge from the drillholes most affected by magmatic influx would be about 4.10^{-2} in the vaporized fluid. The temperature necessary for reaction (1) to proceed at $X_{\text{CO}_2} = 8.10^{-5}$ – 4.10^{-2} is 400–450 °C.

The temperature adjacent to a 2-m thick dyke at 1200 °C rises by 665 °C (see Jaeger, 1957) and a rise by 600 °C persists for about a month at the contact if cooling is only by conduction. In the geothermal area the rise in temperature would be much lower as heat would be required to vaporize the pore water. The resulting temperature would depend on the water content of the adjacent rock and its original temperature. At the dyke border the temperature could easily rise to 500 °C or more, but one would not expect supercritical vapour to persist within the system for any length of time. A convecting fluid would quickly even out a local heating near cooling intrusives. However, this depends very much on aquifer geometry. Heating can occur at one place while high-pressure steam collects at another. The area is crowded with small phreatic craters suggesting that impervious strata may have allowed high pressure to build up locally before a violent outburst. Some of the altered and cemented tuff beds can be fairly impermeable. Supercritical conditions could also be created in pockets between branched dykes.

A contact-metamorphic origin seems to be possible for wollastonite within the geothermal system and is the only acceptable origin in the upper 1000 m in the Krafla geothermal area as deduced from experimental results. Below 1000 m in the formation the origin of wollastonite seems more questionable. The rock temperature exceeds 300 °C below 1000 m. Lithological or structural evidence supporting a contact metamorphic origin for wollastonite is rare. As intrusive rocks have become much more common at this depth a direct correlation might be more difficult.

The temperature of the fluid in this part of the section is only 50–100 °C lower than the experimentally found minimum temperature of formation of wollastonite by reaction (1). At this temperature calcite is no longer a stable hydrothermal precipitate and consequently wollastonite is not formed by reaction (1). The main calcium silicate minerals found that are stable at temperatures exceeding 300 °C are prehnite and epidote. The Ca^{2+} and SiO_2 contents are also controlled by equilibria with other minerals such as quartz, plagioclase, actinolite, and chlorite. Wairakite is stable to temperatures just exceeding 300 °C. The formation of wollastonite is related to equilibria with one or more of those minerals, irrespective of whether it forms by contact metamorphism or hydrothermal

precipitation. Several reactions can be postulated, such as:



Direct precipitation from a hydrothermal fluid is also possible:



A calculation of the mineral equilibria is hampered by the scarcity of thermodynamic data at temperatures exceeding 300 °C. Further, no analyses are available of the pure discharge from aquifers yielding fluids of temperature higher than 300 °C. The discharge from most drillholes is a mixture of waters from shallow and deep aquifers. Ármannsson (pers. comm.) has calculated lower aquifer water composition in the discharge from four drillholes in Krafla. Plots of log *K* versus temperature for reactions (4) and (5) was calculated and is shown in fig. 5*a* and *b*. The corresponding activity products in the calculated lower aquifer waters are shown for comparison.

The composition of the fluid appears not to have any relation to reaction (4). The waters are near to equilibrium with wollastonite according to reaction (5) at 300–350 °C.

Conclusion. Wollastonite is commonly found in subsurface rocks in the Krafla geothermal area, but has not been found elsewhere in Iceland. The main reason is that this area is much more active volcanically than other geothermal areas yet drilled. In the upper 1000 m of the geothermal area in Krafla, wollastonite forms locally as a contact-metamorphic product around dykes at the expense of hydrothermal precipitates. Other typical skarn zone minerals such as andradite, hypersthene, and magnetite sometimes occur together with the wollastonite.

Below 1000 m depth wollastonite occurs much more frequently than at shallower levels. Intrusions are more common below 1000 m depth than above. Contact metamorphic effects would thus be expected to be more significant at that depth. Calcite becomes rarer at the high temperatures below 1000 m depth and the formation of wollastonite would be more likely to be connected to Ca-silicate minerals than calcite.

The calculated composition of the deep waters at 300–350 °C suggests that wollastonite could precipitate directly from the geothermal fluid. The origin of wollastonite below 1000 m depth in the Krafla area could thus be partly hydrothermal and partly contact-metamorphic. The volcanic interaction could also have a catalytic effect on the hydrothermal precipitation of wollastonite.

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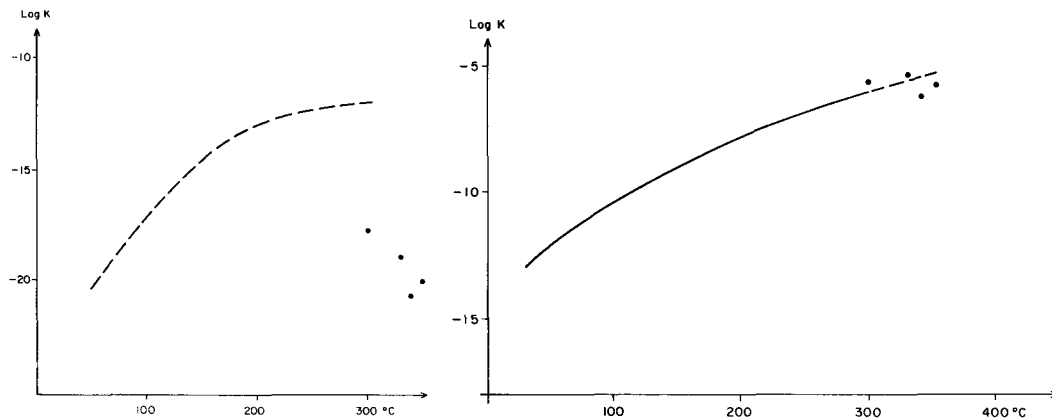


FIG. 5. Log *K* against temperature in °C for the reactions: (a, left) $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O} + 2\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaSiO}_3 + \text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 4\text{H}^+$ and (b, right) $\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 \rightleftharpoons \text{CaSiO}_3 + \text{H}_2\text{O} + 2\text{H}^+$. Thermodynamic data used for the calculation from: Helgeson, 1969; Zen, 1972; and Handbook of thermodynamic data, 1974. Also shown (as black dots) are the corresponding activity products in calculated lower aquifer waters from four Krafla drillholes.

REFERENCES

- Björnsson, A., Johnsen, G., Sigurðsson, S., Thorbergsson, G., and Tryggvason, E. (1979). *J. Geophys. Res.* **84**, 3029-38.
- Browne, P. R. L. (1977). NZGS. *Unpublished report M 58*.
- Greenwood, H. J. (1967). *Am. Mineral.* **52**, 1669-80.
- Handbook of Thermodynamic data, 1974. *Geol. Surv. Nat. Techn. Inform. Serv. U.S. Dept. of Commerce*.
- Harker, R. I., and Tuttle, O. F. (1956). *Am. J. Sci.* **254**, 239-56.
- Helgeson, H. C. (1969). *Ibid.* **267**, 729-804.
- Jaeger, J. C. (1957). *Am. J. Sci.* **255**, 306-18.
- Kristmannsdóttir, H. (1979). *Proc. Sixth Int. Clay Conference, Oxford, 1978*. 359-67.
- Lazarev, A. N. (1972). *Vibrational spectra and structure of silicates*. C/B, Consultant Bureau, New York, London.
- Thompson, A. B. (1971). *Contrib. Mineral. Petrol.* **33**, 145-61.
- Zen, E. (1972). *Am. Mineral.* **57**, 524-53.

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