Wollastonite: First recording in Iceland.

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FORORĐ.

Wollastonít fannst í fyrsta sinn 1975 í bergi frá Kröfluborholu,en hefur ekki fundist áður í íslensku bergi. Þessi steind hefur síðan fundist í flestum borholanna,sem síðar hafa verið boraðar í Kröflu. Fundur steindarinnar þykir það merkur að rétt sé að skýra frá honum á alþjóðlegum vettvangi,þótt núverandi gögn leyfi ekki fullnaðartúlkun á uppruna lennar.

Þessi skýrsla er fyrst og fremst samin til dreifingar til annarra jarðefnafræðinga til að fá athugasemdir við hana áður en gengið verður endanlega frá grein um efnið.

ABSTRACT

Wollastonite is found in hydrothermally altered basaltic rocks in the Krafla high-temperature geothermal area, northern Iceland. This is the first recording of wollastonite in icelandic rocks. The wollastonite is commonly associated with quartz and calcite. A relation between the occurrence of wollastonite and intrusive activity is often clearly demonstrated. A hydrothermal origin of wollastonite at great depths is also suggested.

INTRODUCTION

The Krafla geothermal area is situated centrally within a caldera collapse connected with an active central volcano.

The area has been very active tectonically the last four years and three volcanic eruptions have occurred during this time (Björnsson et al.1978). In historical time one similar major volcanic and tectonic event is recorded.

Twelve deep drillholes (1150-2200 m) have been drilled into the geothermal area in the years 1974-1978. From the subsurface geology it is obvious that intrusive activity has been intensive in the area. The underground rocks (Fig. 1) are tholeiitic basalt lavas and hyaloclastite ridge formations in the uppermost 800-900 m. Below basalt lavas are predominant. Dikes are common. The frequency of intrusive rocks increases by depth and below 1200-1500 m they are predominant in the stratigraphic profile.

The rocks are heavily altered by the hydrothermal solutions.

A regional alteration zoning is found by increasing temperature and depth (see Kristmannsdóttir 1978).

The maximum temperature measured in the drillholes just exceeds $340\,^{\circ}\text{C}$ at 2000 m depth. In zones of lower permeability the rock temperature is close to the boiling point of water at the corresponding pressure. The geothermal fluid at depth is assumed to be neutral to slightly alkaline (pH \simeq 7) with a high CO₂ content (table 1).

During the recent volcanic activity the CO₂ content has increased drastically, 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.

OCCURRENCE OF THE WOLLASTONITE

The wollastonite forms aggregates of fibrous small crystals. A genetic relationship to calcite or quartz is often observed (Fig. 2). Commonly observed are Quartz or calcite vein fillings which are partly converted into 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 prevailent rock temperature at the shallowest depths where wollastonite occurs (600 m) is about 200°C. At those depths the wollastonite is confined to narrow zones and is not found scattered between. The wollastonite is here almost exclusively found in the neighborhood of dikes. In a few of the contact metamorphosed vein fillings andratite garnet, hypersthene and magnetite are found together with the wollastonite.

The wollastonite occurs more frequently by increasing rock temperature and depth. At greater depths (below 1000 m and at rock 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 by 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 analyse was therefore not possible. Powder samples were run on a Guinier de Wolf camera. In table 2 is shown the diffraction pattern of the wollastonite. Some of the first X-ray runs indicated

the presence of the monoclinic parawollastonite form.

Later analyses of purified samples have not confirmed
this. Possibly both forms might be present some places,
but the samples chosen for runs on the Guinier de Wolf camera
have proofed to be wollastonite.

The infra-red absorption spectra of the wollastonite (Fig. 3) identifies it as a β -wollastonite (see Lazarev, 1972). As crystal flakes immersed in oil tend strongly to orient along the best cleavage (100) only one mean refractive index was determined; n = 1,618.

Several chemical analyses have been run of the wollastonite on microprobe (table 3). All show a fairly pure wollastonite. The totals are in all cases rather low, even when a low power and broadened beam was used. This could be due to hydration in the fine grained aggregates or because of poor polishing of this soft material.

ORIGIN OF THE WOLLASTONITE

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

CaCO₃ + SiO₂ \Leftarrow CaSiO₃ + CO₂ (1) (Harker and Tuttle, 1956, Greenwood, 1967, Thompson, 1971) a minimum temperature of formation of wollastonite is inferred to be about 400°C at $X_{CO_2} = 0$ and 1Kb total pressure. The formation temperature rises rapidly by increased mole fraction of CO₂.

Experimentally determined mineral equilibria often tend to lie at considerably higher temperatures than the minerals are found to be formed at in nature. A hydrothermal formation of wollastonite at about 350°C would thus not be surprising, but a formation temperature far below 300°C is considered improbable. A contact metamorphic origin of wollastonite within the geothermal system is thus enforced. 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 CO2 in the totally vaporized hydrothermal fluid would be about $8 \cdot 10^{-5}$ - $4 \cdot 10^{-4}$. Volatilaziation from the magma would change this relation. The CO2 in the discharge from the drillholes most affected by magmatic influx would be about $4 \cdot 10^{-2}$ in the vaporized fluid. The temperature necessary for reaction (1) to proceed at $X_{CO_2} = 8 \cdot 10^{-5} - 4 \cdot 10^{-2}$ is 400-450°C.

This temperature would probably have to persist for a few days.

The temperature adjacent to a 2 m thick dike at 1200°C rises by 665°C (see Jaeger, 1957) and a rise by 600°C persist for about a month 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 dike boarder the temperature could easily rise to 500°C or more, but one would not expect supercritical vapor to persist within the system for any length of time. A convecting fluid would quickly even out a local upheating near to cooling intrusives. However the area is crowded with small explosive craters suggesting that locally imperveous strata may have allowed high pressure to build up 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 dikes.

A contact metamorphic origin seems to be the only acceptable explanation of the formation of wollastonite in the upper 1000 m in the Krafla geothermal area.

Below 1000 m in the formation the origin of wollastonite seems more questionable.

In this part of the section the rock temperature is 300-350°C. Calcite is no longer a stable hydrothermal precipitation and consequently wollastonite is not formed by reaction (1).

Lithological or structural evidences supporting a contact metamorphic origin of wollastonite are rare. As intrusives have become much more frequent 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).

The main calcium silicate minerals stable at temperatures exceeding 300°C are prehnite and epidote. The Ca²⁺ and SiO₂ contents are also controlled by equilibria with other minerals as quarts, plagioclase, actinolite and chlorite. Wairakite is stable at temperatures just exceeding 300°C. The formation of wollastonite is related to equilibria with one or more of those minerals irrespective if it forms by contact metamorphism or hydrothermal precipitation. Several reactions can be postulated as:

prehnite clinozoizite (2) $3Ca_2 Al_2 Si_3 O_{10} (OH)_2 \Rightarrow 2Ca_2 Al_3 Si_3 O_{10} (OH)$ wollastonite + $2Ca SiO_3 + H_4 SiO_4 + 2O_2$

- (3) prehnite anortite wollastonite $Ca_2 Al_2 Si_3 O_{10}$ (OH) 2 $Ca Al_2 Si_2 O_8 + Ca SiO_3 + H_2O_8$
- (4) wairakite wollastonite Ca Al₂ Si ₄ O₁₂ · 2H₂O + 2Ca²⁺+H₂O \rightleftharpoons Ca SiO₃ + prehnite Ca₂ Al₂ Si₃ O₁₀ (OH)₂ + 4H⁺

A direct precipitation from a hydrothermal fluid is also possible:

(5)
$$Ca^{2+} + SiO_2 + H_2O \implies Ca SiO_3 + 2H^+$$

A calculation of the mineral equilibria is hampered by the shortness of thermodynamic data at temperatures exceeding 300°C. Further, no analysis are available of the pure discharge from aquifers yielding fluids of temperature higher than 300°C. The discharge from most drillholes is a mixture from shallow and deep aquifers.

Mineral equilibria have been calculated for reactions (4) and (5) at temperatures $60\,^{\circ}\text{C}$ to $300\,^{\circ}\text{C}_{\epsilon}$

The calculated activity product of $\frac{\int H^{+}J^{2}}{\left[\operatorname{Ca}^{2}\right]}$ in selected

analyses of discharge from drillholes yielding from only one aquifer or aquifers at a restricted depth interval is also shown for comparison (Fig. 4).

The composition of the fluid appears not to be governed by those mineral equilibria at and below 300°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 into.

Wollastonite is not a stable hydrothermal mineral in the upper 1000 m of the geothermal area in Krafla, but has formed locally around dikes at the expense of hydrothermal precipitations.

The high rock temperature below 1000 m in the geothermal system suggests a possible hydrothermal formation of wollastonite; especially as no geological evidences support a contact metamorphic origin. From the available data the mechanism of wollastonite formation below 1000 m depth cannot be surely established.

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

	1	2	3	4
pH/°C	6,96/206,4	6,74/224,9	6,63/205	7,12/303
\$ i02	300,13	373,92	387,30	681
Na ⁺	151,64	152,10	205,56	143
K+	11,75	19,28	16,41	20,2
Ca ²⁺	2,10	2,62	3,44	1,1
Mg ²⁺	0,03	0,01	0,04	0,02
so ₄ 2-	157,43	177,45	217,03	73,1
Cl-	23,69	26,79	27,35	11,8
F	0,46	0,00	0,57	0,46
H ₂ S tot	63,38	14,97	67,07	92,4
CO ₂ tot	271,74	543,20	458,25	10013

NEA data.

The temperature is silica temperature.

The composition of deep water composition is calculated from analyses of collected water and gases assuming inflow from one aquifer. Sample 3 is a mixture of shallow and deep aquifers.

TABLE 2

X-ray diffraction pattern of powder samples of wollastonite from Krafla (mean values).

d in Å	relative intensity	d in Å	relative intensity
7,65	m	2,17	m
3,84	S	2,03	Ŋ
3,32	VS	1,98	VW
3,08	S	1,92	VV
2,97	VS	1,76	m
2,81	VW	1,72	m
2,72	WV	1,61	m
2,55	W	1,53	W
2,47	m	1,48	m
2,34	m	1,36	m
2,30	m		

vs: very strong

s: strong

m: medium strong

w: weak

vw: very weak

TABLE 3

Microprobe analyses of wollastonite from the hydrothermally altered rocks in Krafla

	1	2	3	
Weight	%			
${ m SiO}_2$	50,14	49,83	48,74	
TiO2		0,07	-	
Al_2O_3	0,08	0,10	0,08	
Fe0	0,28	0,25	0,02	
MnO	0,22	0,19	0,11	
MgO	0,04	0,06	0,02	
Ca0	43,85	46,80	47,47	
Na_2O	0,01	0,02	0,01	
K ₂ 0	0,02	0,02	-	
	georgescheiden der gefrächte von Antherson aus			
total	94,64	97,34	96,45	

- not detected

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ORKUSTOFNUN Jarohitadeild Gróf tenging milli helstu berg-Krafla myndana, sem borholur KG-8-KW-I skera F. 16163 FIG.1 Dýpi í m SA NS O (480my.s) - 100 Formation - 200 - 300 Hyaloclastite - 400 - 500 - 600 - 700 Lava Formation - 800 - 900 - 1000 -1100 Intrusive Formation - 1200 - 1300 -1400-1500- 1600 -1700 -1800 Drillholes - 1900 Basalt lava altered Basalt lava fresh -2000Hyaloclastite -2100 Breccia, Basait rich -2200 Dolerite Granophyre.... 400 600 1000 200 oós >Dykes

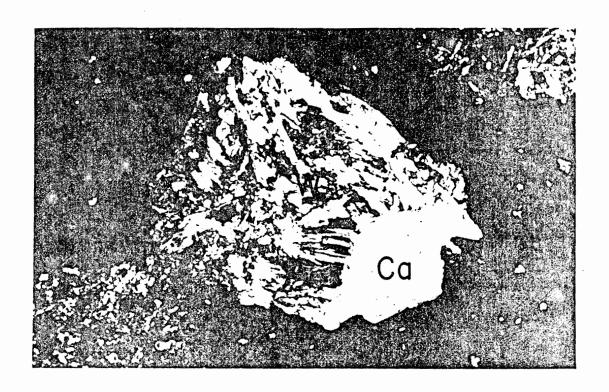
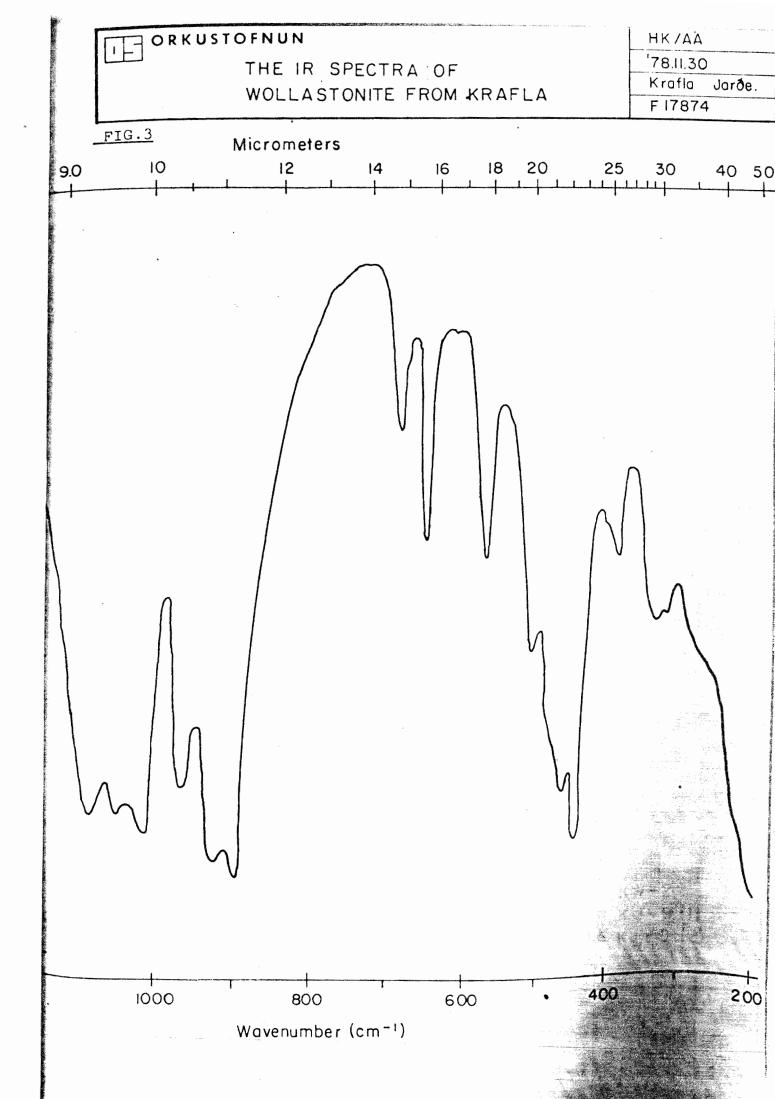
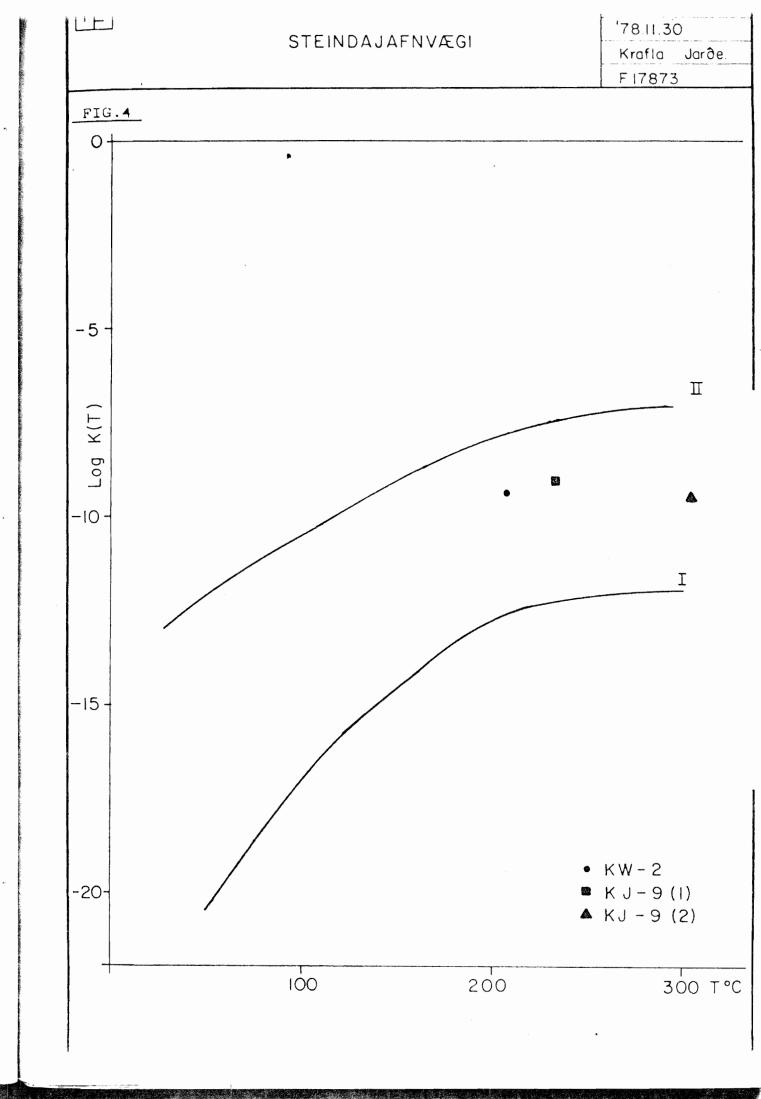


Fig.2.





Legend to figures.

- Fig. 1. Stratigraphic section through the Krafla geothermal area.
- Fig. 2. Wollastonite (W) growing on expense of calcite (Ca). Magnification 80x.
- Fig. 3. The infrared spectra (far-infrared part) of wollastonite from 830 m depth in drillhole KJ-11 in Krafla.

Fig. 4.

Log K against temperature for the reactions:

wairakite

wollastonite

I: CaAl₂Si₄ O₁₂ 2H₂O + 2Ca⁺+H₂O **⇒** CaSiO₃ prehnite + Ca₂Al₂Si₃O₁₆ (OH)₂+4H⁺ .

and

II: $Ca^{2+} + H_4SiO_4 \implies CaSiO_3 + H_2O + 2H^+$

The calculated $\frac{[H^+]^2}{[Ca^2^+]}$ for

discharge from selected drillholes is shown for comparison. Thermodynamic data used for the calculation from: Helgeson, 1969, Zen 1972 and Handbook of thermodynamic data, 1974.