14. K. Mogi, *Bull. Earthquake Res. Inst. Tokyo Univ.* **36**, 99 (1958); J. B. Walsh and R. W. Decker, *J. Geophys. Res.* **76**, 3291 (1971).
15. Gudmundur Kjartansson, *Geological Map of Iceland* (Museum of Natural History, Reykjavik, 1962), sheet 6.

16. We thank J. Peirce, W. Walker, and J. Decker for their assistance with the fieldwork, Gudmundur Sigvaldason and Gudmundur Pálmason for their continuing help and advice, and V. McGee for his aid with the statistical tests. Supported by the American Philosophical Society and NSF grants GA-965 (1967) and GA-2686 (1970).

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Quartz: Synthesis at Earth-Surface Conditions

Abstract. *Quartz has been crystallized directly from seawater at room temperature. This is the first time that identifiable quartz has been synthesized in aqueous solution at earth-surface conditions without the aging of an original amorphous precipitate. The concentration of dissolved silica in equilibrium with quartz at 20°C and 1 atmosphere is 4.4 ± 0.3 parts per million, a value in agreement with the theoretical value obtained by a constant heat capacity fit of higher temperature equilibrium data. This experiment confirms the results of petrologic investigations which suggest that quartz precipitates directly from aqueous solution during chemical weathering and early diagenesis.*

Quartz has been considered to be chemically "inert" in most environments at or near the earth's surface. It has been assumed that, at temperatures below 100°C, the formation of quartz from supersaturated solutions or from amorphous silica requires thousands of years. The dissolution of quartz in unsaturated solutions at most earth-surface conditions is slow (*1*, *2*). However, quartz-cemented sandstones, secondary quartz rimming of Recent lacustrine quartz sands, and quartz crystals found in weathering profiles are interpretable as precipitates of quartz from aqueous solution at earth-surface conditions formed in a relatively short time (*3*).

Recently, quartz has been synthesized over the temperature range from 0° to 80°C by the aging of amorphous hydroxide-silica precipitates of iron (Fe^{3+}) and other elements in the presence of aqueous solutions (*2*). Morey *et al.* (*4*) obtained supersaturated solutions of silica by the continuous agitation of a suspension of quartz grains in water. In one experiment the solution reached a concentration of 80 parts per million (ppm) of dissolved silica after 386 days of agitation, and subsequently the concentration dropped

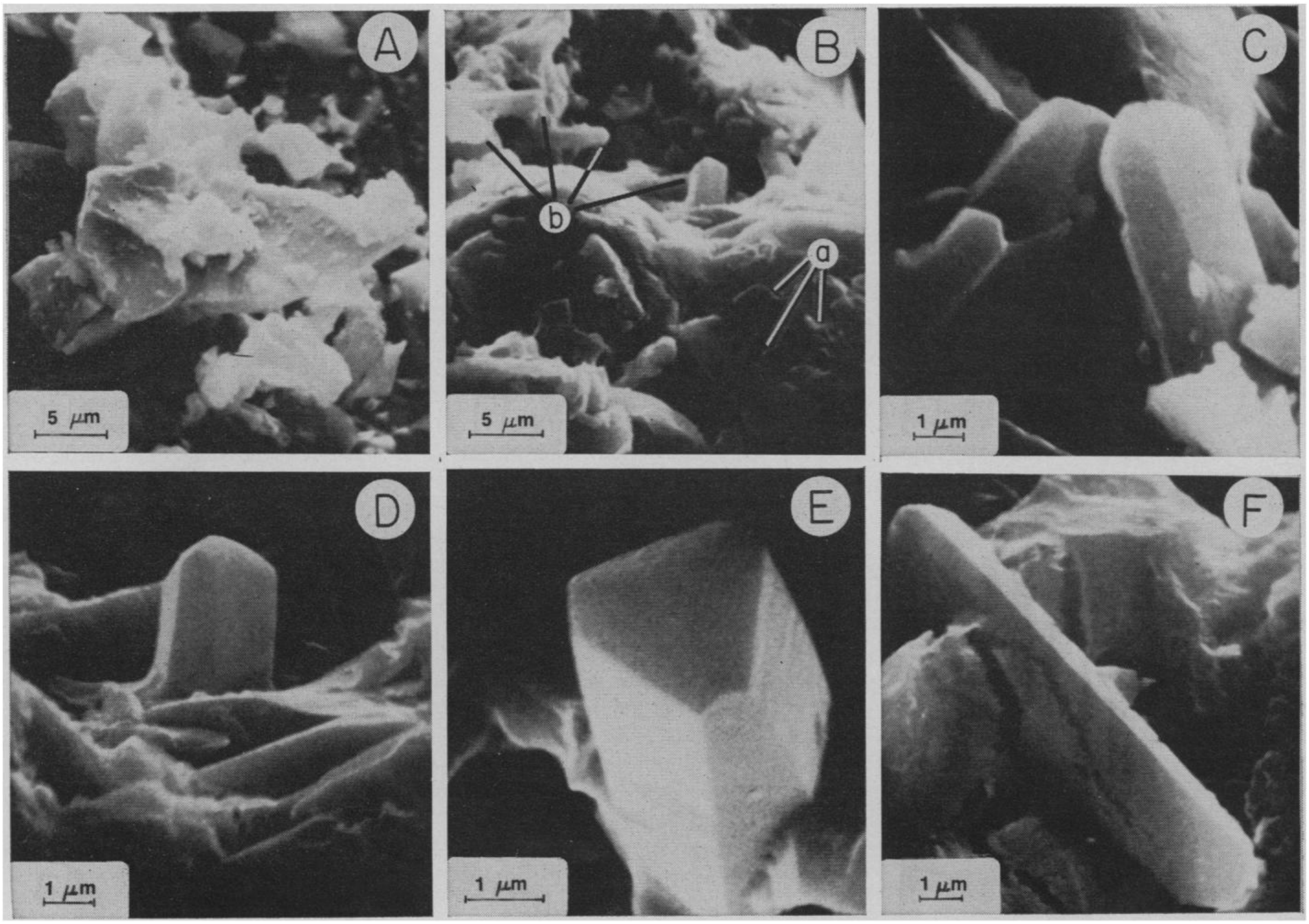

Fig. 1. Scanning electron photomicrographs. (A) Ground quartz material obtained by grinding a single crystal of quartz. Note the high angularity and poor sorting of the particles. (B) On the surface of the ground quartz material after reaction, V-shaped solution pits (*a*) have developed. Several authigenic quartz crystals (*b*) are seen in the upper portion of the photograph. (C) Authigenic quartz crystals converging toward the center of the photomicrograph. (D) Crystal of authigenic quartz developed on a conchoidal breakage pattern of the ground material. (E) Authigenic quartz displaying striations parallel to (0001) on the prism faces and the tapering of a $10\bar{1}0$ prismatic face. (F) Authigenic quartz crystal with double terminations, about 10 μm in length.

to 6 ppm within 30 days. Morey *et al.* concluded that quartz was precipitated from the solution and that it has a maximum silica solubility of 6 ppm at 25°C and 1 atm. We have synthesized quartz crystals directly from aqueous solution at earth-surface conditions within 3 years.

In a continuing study of the controls of seawater composition, Mackenzie and his associates initiated some experiments in which the reactivity of silicate minerals in silica-deficient and silica-enriched seawater was determined (*5*). During the course of the experiments, 1 g of quartz from a crystal ground to < 62 μm was placed in a polyethylene vessel containing 200 ml of seawater low in dissolved silica (0.03 ppm), freshly collected from Ferry Reach, Bermuda. The seawater was initially filtered through a 0.45-μm Millipore filter, and several drops of a bacteriacide (Quatam D) was added to prevent biologic activity. The container was continuously agitated at 20°C on a shaker table for 12 months. During this time aliquots were withdrawn each month and analyzed for dissolved silica by the colorimetric method of Mullin and Riley (*6*). The container was then removed from the shaker table. After a period of 2 years, the *p*H and dissolved silica content of the seawater were measured and the silica grains were removed from the seawater with a pipette. Surface textures of the grains were subsequently investigated by means of a scanning electron microscope (SEM) (Jeolco).

During the course of reaction with ground quartz, the silica concentration of the seawater rose to about 3 ppm in 1 month and to 4.4 ppm within 1 year. No large degree of supersaturation of the seawater with respect to quartz was observed during the course of the experiment. The final measured silica content of the seawater was 4.4 ppm, which, within the precision of the analytical technique ($\pm$ 0.3) is equivalent to the predicted solubility of quartz under the experimental conditions of 20°C and 1 atm (*4*, *7*). The *p*H of the seawater remained at 8.1 $\pm$ 0.1 during the 3-year period.

In Fig. 1 scanning electron photomicrographs depict several aspects of the development of authigenic quartz. The pictures show that quartz crystals grew on the surfaces of the original ground quartz material during reaction with seawater. Fourteen SEM pictures of three individual aliquots of the original quartz material were taken. Figure 1A illustrates the starting material, ground quartz, which exhibits poor sorting, high angularity, and no evidence of external crystal morphology. Figure 1, B to F, shows the quartz surfaces after immersion in seawater and illustrates the formation of newly formed crystals. All 60 SEM pictures of four individual aliquots taken after reaction showed many crystals on ground quartz surfaces. To preclude the possibility that the crystals are a carbonate mineral, some quartz surfaces were analyzed by scanning electron microscopy after treatment in a 10 percent HCl solution. Newly formed crystals were still present on the ground quartz after acid treatment. Acid treatment also precludes the possibilities that the crystals are apatite, which will dissolve in HCl, or zeolite, which will decompose in HCl. X-ray diffraction analysis showed only quartz present after reaction.

The crystals appear to be quartz, as evidenced by crystal morphology—hexagonal, elongate, prismatic forms with $(10\bar{1}0)$ faces horizontally striated and terminated by two rhombohedrons (see Fig. 1, E and F). Crystal faces commonly are tapered toward the least developed rhombohedral termination. Figure 1E illustrates the tapered shape of a $(10\bar{1}0)$ face. In this example, the crystal is probably terminated by two poorly defined rhombohedrons; however, it is also possible that the termination is a basal pinacoid, a less characteristic crystal form for quartz. Figure 1D illustrates a quartz crystal growing on a conchoidal fracture surface of ground quartz.

It is likely, as suggested by Morey *et al.*, that high surface energies were present on portions of the original quartz grains owing to their angularity and small size and to stresses imparted to the grains by grinding. During the course of the reaction, silica dissolved more readily from the more reactant surfaces and sites of the grains, giving rise to the formation of such surface textural features as V-shaped pits (Fig. 1B). The silica concentration in seawater climbed to slightly over 4.4 ppm; nucleation of quartz crystals on ground quartz surfaces then occurred. The growth of the quartz took place at a steady-state silica concentration just above the quartz saturation point; that is, the growth rate of quartz was greater than the rate of dissolution of the disturbed layer.

Morey *et al.* obtained 6 ppm as the solubility of quartz at 25°C, on the assumption that the decrease in silica concentration in their supersaturated solution reflected the crystallization of quartz. However, they did not document the growth of crystals. The first ionization constant for H_4SiO_4 is relatively negative, $K = 10^{-9.9}$, and the activity coefficients of neutral species in a solution with the ionic strength of seawater are approximately equal to unity. Consequently, the value of 4.4 ppm, $10^{-4.13}$ mole per 1000 g of H_2O, at 20°C is the equilibrium H_4SiO_4 activity because (i) at the *p*H of our experiment, $H_3SiO_4^-$ is an unimportant species in solution, and (ii) the concentration of silica in seawater is very nearly equal to its activity. The H_4SiO_4 equilibrium activity at 20°C is in agreement with that predicted thermodynamically from the value of Morey *et al.* at 25°C; thus, a free energy of formation of -204.6 kcal mole^{-1} for quartz and -312.6 kcal mole^{-1} for $H_4SiO_{4(aq)}$ at 298°K and 1 atm now seems to be indisputable.

Our experiment suggests that quartz growth in nature may occur in relatively short intervals of time, provided saturation is reached. Disturbed surfaces on quartz grains can form in several different environments, for example, beach, glacial, and metamorphic environments. Dissolution of these metastable surfaces in natural waters could lead to saturation and precipitation of quartz. Also such active surfaces and sites could provide nuclei for the epitaxial growth of new crystals as well. It is possible that quartz surfaces need to be free of sorbed materials such as organic films or iron oxides, as was the case in our experiment, in order for quartz to nucleate on these surfaces; if so, the growth of quartz in nature at earth-surface conditions may be inhibited owing to the coverage of quartz grains by organic or inorganic coatings.

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References and Notes

1. O. P. Bricker and R. M. Garrels, in *Principles and Applications of Water Chemistry*, S. D. Faust and J. V. Hunter, Eds. (Wiley, New York, 1967), p. 449; R. M. Garrels and F. T. Mackenzie, in *Equilibrium Concepts in Natural Water Systems*, W. Stumm, Ed. (American

Chemical Society, Washington, D.C., 1967), p. 222.
2. H. Harder and W. Flehmig, *Geochim. Cosmochim. Acta* **34**, 295 (1970).
3. E. C. Dapples, personal communication; R. Siever, in *Silica in Sediments*, H. A. Ireland, Ed. (S.E.P.M. Spec. Publ. No. 7, Society of Economic Paleontologists and Mineralogists, Tulsa, Okla., 1959), p. 55.
4. G. W. Morey, R. O. Fournier, J. J. Rowe, *Geochim. Cosmochim. Acta* **26**, 1029 (1962).
5. F. T. Mackenzie and R. M. Garrels, *Science* **150**, 57 (1965); ——, O. P. Bricker, F. Bickley, *ibid.* **155**, 1404 (1967).
6. J. B. Mullin and J. P. Riley, *Anal. Chim. Acta* **12**, 1962 (1955).
7. H. C. Helgeson, *Am. J. Sci.* **267**, 729 (1969). The equilibrium amount of dissolved silica at 20°C was obtained by a constant heat capacity fit of higher temperature log *K* values.
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Ultrahigh-Frequency Electromagnetic Fields for Weed Control: Phytotoxicity and Selectivity

Abstract. *An ultrahigh-frequency electromagnetic field (2450±20 megahertz) is lethal to plants and seeds of several species after relatively short exposure times. Some species are highly susceptible; others are relatively resistant to a given field intensity. Phytotoxicity is increased in imbibed seeds and young plants. It is decreased in dry seeds and sometimes decreased in mature plants. Soil partially attenuates the field but is not opaque to it.*

The use of ultrahigh-frequency (UHF) electromagnetic field of frequency 2450 ± 20 Mhz for vegetation control and its potential to discriminate between species are considered in this report. The influence of imbibition of the seed, the stage of development of the plant, and presence or absence of soil on phytotoxicity may be important parameters in the effective use of UHF fields for weed control. Accordingly, the following work investigates the influence of each of these on phytotoxicity.

The frequency used in this experiment is in the microwave region of the radio-frequency band (*1*). In this region the absorption occurs principally by changes in the rotational energies of molecules in the object being exposed. The absorption of electromagnetic energy by rotations is the result of an interaction of the molecular dipole moment with the electromagnetic field. The molecule must have a permanent dipole moment to exhibit absorption in this frequency range.

Various workers have reported that macrowave, or lower-frequency fields (10 to 100 Mhz), increase germination and alter subsequent growth of crop species (*2*). It is interesting to note that application of macrowave fields to insects results in a method of control. Nelson (*3*) states that the mechanism of lethal action has not been explained with any certainty, and there may be physiological lesions other than thermal effects that contribute to the death of insects in a radio-frequency field. Two investigations on effects of low-frequency fields on weed seeds were reported in 1950 and 1954 (*4*), but the methods used did not permit conclusive results.

The UHF range has not previously been studied for weed control. Recently UHF fields have been studied for

Table 1. Relative germination or seedling survival* of several species after exposure to radiation at three stages of development. Numbers followed by the same letter are not significantly different at $P < .05$ by Duncan's test.

Species	Dry seed (%)		Wet (4-hour imbibed) seed (%)		Germinating (46-hour) seed (%)	
	At 45 joule/g	At 270 joule/g	At 23 joule/g	At 45 joule/g	At 23 joule/g	At 45 joule/g
Corn *(Zea mays)*	73abc	15f	26bcd	1	52ab	1
Cotton *(Gossypium hirsutum)*	73abc	72ab	13cd	1	21abc	0
Soybean *(Glycine max)*	71abc	70abc	28bcd	0	31ab	0
Sorghum *(Sorghum vulgare)*	88a	54bc	22bcd	1	62a	15
Wheat *(Triticum vulgare)*	100a	48cde	37bc	0	48ab	15
Peanut *(Arachis hypogaea)*	100a	83a	53ab	0	46ab	0
Honey mesquite *(Prosopis juliflora)*	59c	48bc	1d	1	16c	0
Cucumber *(Cucumis sativus)*	93a	69ab	47b	1	31ab	1
Mustard *(Brassica* spp.*)*	79ab	83a	9cd	0	48ab	0
Curled dock *(Rumex crispus)*	72abc	100a	19bcd	0	56ab	21
Jungle rice *(Echinochloa colonum)*	71abc	75cd	74a	0	48ab	0
Pigweed *(Amaranthus* spp.*)*	74abc	35ef	12cd	0	0c	0

$* \ \frac{\text{Germination of treated}}{\text{Germination of control}} \times 100.$