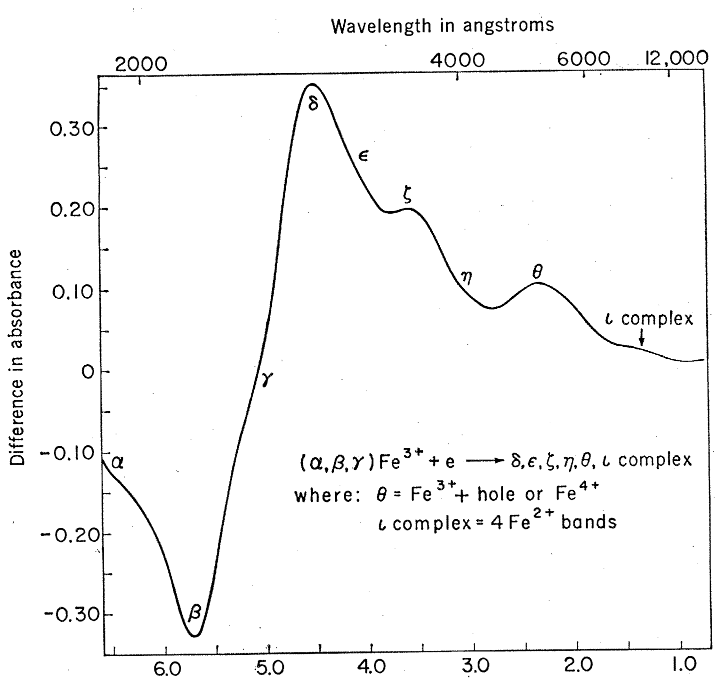
Iron in Synthetic Quartz: Heat and Radiation Induced Changes

Abstract. *As part of a study of the possible changes in silicate material on the lunar surface produced by solar radiation, effects of ionizing radiation, of heating, and of heating followed by ionizing radiation on iron-doped synthetic quartzes have been studied as models. The optical changes are mainly related to valence changes in ferric or ferrous ions.*

Earlier work in this laboratory (*1*, *2*) on iron-containing quartz has been mainly concerned with the effects of x-rays on Fe^{3+} incorporated in substitutional positions in positive rhombohedral growth regions of quartz. The charge compensation for the Fe^{3+} substitution for Si^{4+} is supplied by Li^{+}, Na^{+}, and sometimes H^{+}. In positive rhombohedral growth, x-irradiation leads to the production of color centers in the ultraviolet, visible, and near-infrared regions of the spectrum (*1–3*). Work on natural and synthetic amethyst quartz led to the prediction of models for radiation bleaching of the thin lunar surface layer (*4*). Amethyst quartz usually shows positive rhombohedral growth in nature and is produced synthetically on a positive rhombohedral seed plate. In positive rhombohedral growth, the Fe^{3+} ion is essentia'ly reduced upon x-irradiation, as indicated by the decrease in the height of three Fe^{3+}-related absorption bands and by growth of five color center absorption bands related to iron and of four absorption bands related to Fe^{2+} (*2*, *5*) (Fig. 1). Bleaching of the color centers by heat or by treatment with ultraviolet light restores the original intensity of the Fe^{3+} band. The optical effect is therefore reversible and may be cycled.

Our report concerns the effects of (i) x-ray treatment at room temperature, (ii) heating, and (iii) x-irradiation after heating of synthetic quartz grown on a seed cut perpendicular to the optic axis, basal growth. The quartz is grown containing predominantly either Fe^{3+} or Fe^{2+} (with Fe^{3+}) ions as impurities (*6*). X-ray treatment of the Fe^{3+} quartz, cut parallel to the optic axis, shows little effect of the irradiation after 18 hours (45 kv-peak, 35 ma, 5.4 cm from Be window of a Machlett AEG 50T x-ray tube), except for barely preceptible growth of the color center bands and for indication of growth in the vacuum ultraviolet region. When the sample is held at 500°C for 2 hours, there is precipitation of a blue phase that shows a Tyndall effect. The amount of precipitation of a separate phase is correlated to the zones showing the most yellow color, which is due to the Fe^{3+} band. Thus the iron ion is precipitating as a separate phase. This indicates the Fe^{3+} in basal growth is mainly incorporated interstitially, as substitutional iron would be impossible to precipitate (*7*). Blue quartz in nature is probably produced in a similar way.

When the basal-growth synthetic quartz which contains Fe^{2+} and Fe^{3+} is heated to 500°C for 3 hours, the Fe^{2+} is completely oxidized to Fe^{3+}, as shown (Fig. 2) by complete disappearance of the Fe^{2+} bands and growth of bands in the Fe^{3+} optical region. X-irradiation after heating further enhances the Fe^{3+} region (Fig. 2). This is the complete reverse of the effect of x-irradiation on Fe^{3+}-doped positive rhombohedral growth quartz. In the Fe^{2+}-doped quartz, the ferrous ion could have five possible environments as follows: (i) Fe^{2+} substitutional (for Si^{4+}) accompanied by two interstitial alkali ions; (ii) Fe^{2+} substitutional accompanied by an oxygen vacancy; (iii) Fe^{2+} interstitial situated near and furnishing charge compensation for two substitutional Fe^{3+} ions; (iv) Fe^{2+} substitutional accompanied



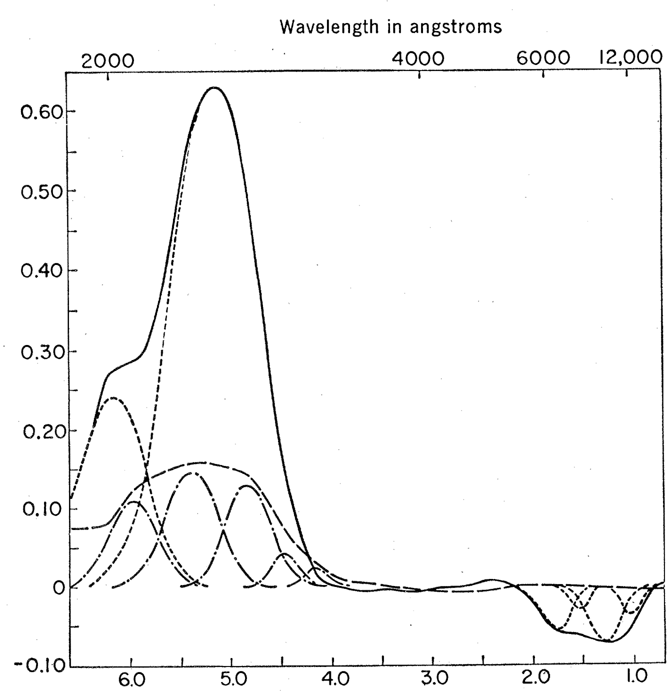


Fig. 1 (left). Synthetic quartz containing Fe^{3+}, positive rhombohedral growth. Specimen cut parallel to $(10\bar{1}1)$. Difference in absorbance before and after 11.1 hours of x-irradiation. Sample thickness, 0.095 cm. Fig. 2 (right). Synthetic quartz containing Fe^{2+}, basal growth. Specimen cut parallel to optic axis. Difference in absorbance: ———, before and after heating at 500°C for 3 hours; – – – –, possible resolution of bands; — — —, after heating and after 62 hours x-irradiation; —.—.—, possible resolution of bands. Sample thickness, 0.085 cm.

by Fe^{2+} interstitial for charge compensation; (v) three Fe^{2+} substitutional accompanied by two Fe^{3+} interstitial for charge compensation. The second case is the least probable because of the partially covalent (about 50 percent) nature of the Si-O bond in the three-dimensional quartz network. Whether Fe^{2+} is substitutional or interstitial remains to be determined.

Thus, while substitutional Fe^{3+} in positive rhombohedral growth is chemically reduced by ionizing radiation and while interstitial Fe^{3+} in basal growth is insensitive and remains essentially unchanged, Fe^{3+} ions produced by heating of Fe^{2+}-doped quartz are further enhanced, rather than reduced, by x-irradiation in some manner not understood. One can conclude that there is a coordination position specificity for sensitivity of the Fe^{3+} ion to ionizing radiation in quartz and that the effect of ionizing radiation depends on whether Fe^{3+} was introduced during growth of the quartz or by oxidation of Fe^{2+} after growth of the quartz. Thus, in quartz the role of Fe^{3+} related to radiation effects is not a simple one, and a complete understanding of the solar wind and of solar radiation effects on the silicate minerals and glasses of the lunar samples may be difficult where, in addition to iron, "smaller amounts of manganese and titanium present may also be important in these reactions" (*4*).

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References and Notes

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6. Synthetic quartzes used in this study were grown as part of an experimental program by B. Sawyer at Sawyer Research Products, Inc., Eastlake, Ohio, and presented to us.
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Insect Flight: Lift and Rate of Change of Incidence

Abstract. *Large changes in lift output result when a simulated insect wing, undergoing a downstroke, is subjected to a dynamic change of incidence. Given a large positive rate of change of incidence, transient lift values several times those realized in steady-state operation at the same angle of incidence are obtained. Thus a means exists by which insects achieve several times the lift expected by conventional quasi-steady considerations.*

The fluid mechanics of lifting surfaces becomes less certain as the surface (i) becomes heavily loaded, (ii) experiences a motion with a large unsteady component, or (iii) moves at a scale neither decidedly viscous nor inviscid. The domain of insect flight embraces all these areas of difficulty. Consequently the bromide concerning the prevalence of "bumble bee" aerodynamics over the pretensions of engineers contains a grain of truth. Performance analyses of several species of beetles (*1*) and *Drosophila* (*2*) reveal a force decrement factor of roughly two or three, that is, the forces necessary for sustenance appear several times larger than those estimated as available, where judgments of force available are based on general steady-state low Re (Reynolds number, or the ratio of inertial to viscous forces) experiments (*3*) or steady tests of a detached wing (*2*). Experiments with a simulated cockchafer, *Melolontha vulgaris* (*4*), indicated a satisfactory agreement between measured lift and insect weight. Whereas the lift was shown to be circulatory in origin and dependent on the degree of unsteady flow, no attempt was made to identify the source of the large requisite force coefficients.

My study concerns influence on lift of a simulated *M. vulgaris* wing. Particular emphasis is placed on those factors capable of producing larger sustaining forces than those revealed in quasi-steady or steady-state analyses. Specifically, the results of wing incidence, rate of change of incidence, and rate of change of downstroke velocity are presented to identify the mechanism by which lift is produced.

The apparatus (Fig. 1) consisted of an articulated single wing mounted so as to flap harmonically through a stroke of 108°. Geared to the flapping drive, a separate cam controlled incidence. A groove machined into the incidence cam moved a follower arm about its pivot, shifting a bobbin along the main square driveshaft. A nylon cord, tied at one location on the bobbin and passing through holes in its opposite side, formed an endless loop that drove the incidence sheave through friction. The latter was directly connected to the wing root. Thus any desired incidence or rate of change of incidence was obtained by cutting an appropriate groove in the incidence cam. As the incidence control arrangement necessarily suffered (i) lost motion due to clearances between components, and (ii) deflection due to operating loads, true values of incidence and rate of change were measured under full load through use of a Strobotac and sighting device.

Mounted in a miniature open-throat wind tunnel, the flapping plane was displaced 60° from the horizontal plane of the tunnel, roughly duplicating the stroke-plane inclination for a forward-flying *M. vulgaris*. Lift values were obtained by measuring the change of momentum of the airstream as it crossed the stroke plane of the beating wing. In this quasi-steady treatment, variations in momentum are averaged over a cycle. Instantaneous values are inappropriate, not only for certain fundamental reasons (*5*), but also because virtual-mass force exists on the instantaneous level. Net virtual-mass force may be shown to be zero over an entire cycle (*6*) even for large-order perturbations. Thus, the use of mean values automatically eliminates all influence of virtual mass.

The expression utilized for generated lift was: lift equals the mass flow through the flapping plane times the downward component of air velocity, specifically, that component normal to the flight path or the wind-tunnel axis. As time-averaged values from a single point in space (0.7 wing radius, mid-downstroke azimuth) were employed, the resulting lift figures reflect the situation during downstroke at a location where lift is near maximum.

In practice, the sensor of a commercial hot-wire anemometer was positioned on the upwind and downwind sides of the flapping plane to obtain the local induced-velocity data. Calibration was obtained with a whirling arm arrrangement. Triggered at the start of downstroke, the hot-wire trace was