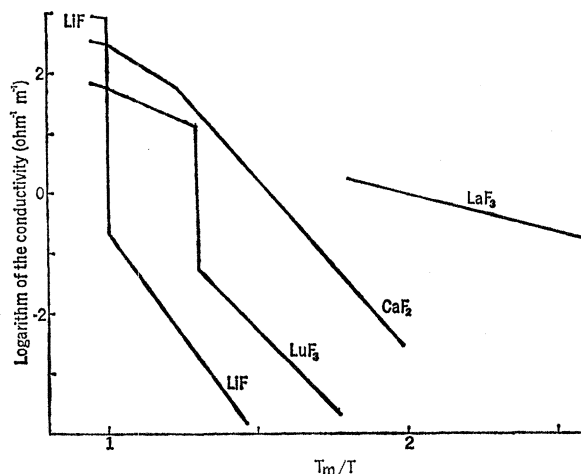


Fig. 2. The logarithms of the specific conductivities of LiF (3), LuF₃ (this report), CaF₂ (9, 10), and LaF₃ (6) as a function of the quantity (melting temperature/temperature).



the transition being accompanied by an entropy increase comparable to the entropy of fusion and by an increase of several orders of magnitude in the ionic conductivity. In this report YF₃ and LuF₃ are shown to behave in the same way.

The trifluorides of Y and the heavier rare-earth elements are known (4) to undergo a transformation from an orthorhombic to a hexagonal structure on increasing temperature. In LuF₃ and YF₃ the entropy of the solid-state transition is comparable to the entropy of fusion (5). As high fluoride ion conductivity is common in the fluorides of the alkaline-earth and rare-earth elements (6), solid electrolyte behavior in YF₃ and LuF₃ might be predicted.

Conductance measurements were made with a universal bridge operated at 1 to 10 khz. Samples were made by freezing a melt of the salt (7) in a sealed boron nitride crucible under a purified Ar atmosphere. Two Pt wires dipping into the crucible served as electrodes.

The results of a large number of measurements are shown in Fig. 1, where, for convenience, the logarithm of the conductivity is shown as a function of reciprocal temperature. Because the data are so numerous, individual points are not shown. The conductance behavior of a sample was very reproducible except in the region of the solid transformation. However, the absolute value of the conductivity is subject to a constant error, perhaps as large as a factor of 2, arising from uncertainty in the cell constant, but this is unimportant in the present context. Hysteresis in the phase transition was found in every case, but the width of the loops was variable. This observation probably accounts for the wide range

of transition temperatures reported in the literature (4, 5, 8). The transition on heating LuF₃ was very sluggish, and in the transition region the conductivity continued to change over times as long as 24 hours. By way of contrast, the transition on cooling LuF₃ was very sharp and reproducible at 1160° ± 5°K.

As can be seen from Fig. 1, the conductivity of the high-temperature solid phase is close to that of the melt. Indeed, for LuF₃ no discontinuity at the melting point was observed. This parallels the behavior of CaF₂ (9). Clearly, LuF₃ and YF₃ are true solid electrolytes.

The rare-earth fluorides with the tysonite structure, for example, LaF₃ and CeF₃, have relatively high ionic conductivities even at room temperature (6) and approach solid electrolyte behavior well below the melting temperatures. In these materials as well as in CaF₂ (10) the transitions to the highly conducting states are gradual. It is very revealing to plot the conductivities of the different types of salt on a reduced temperature scale, for

example, the logarithm of the conductivity plotted against the quantity (melting temperature/temperature). This is done in Fig. 2 in which the conductivities of LuF₃, LaF₃, and CaF₂ are compared with that of a typical alkali halide, namely, LiF (3). The high conductivities of the fluorides of the larger cations are apparent.

It is interesting that LuF₃ and YF₃ provide rare examples of noncubic ion-disordered solids. Another example, also hexagonal, is high chalcocite, Cu₂S (11).

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Shape and Nature of Small Sedimentary Quartz Particles

Abstract. Quartz particles in sediments become flatter with decreasing size; a cleavage mechanism may operate below the critical size of about 100 microns. Flat particles would tend to form a more open packing than spherical particles, and this may contribute to the collapse of loess and similar soils and the sudden loss of strength observed in "sensitive" clay soils.

It appears that small quartz particles in sediments are almost always shaped like flat plates. Also, they are almost invariably produced by breakage, by attrition from larger particles. If this is so, it suggests that a hitherto unsuspected cleavage mechanism operates in

quartz when the particle size is reduced below a certain critical value. Our observations suggest that this critical size is on the order of 100 μm.

Natural particles with diameters smaller than this critical value have a bimodal distribution and appear as

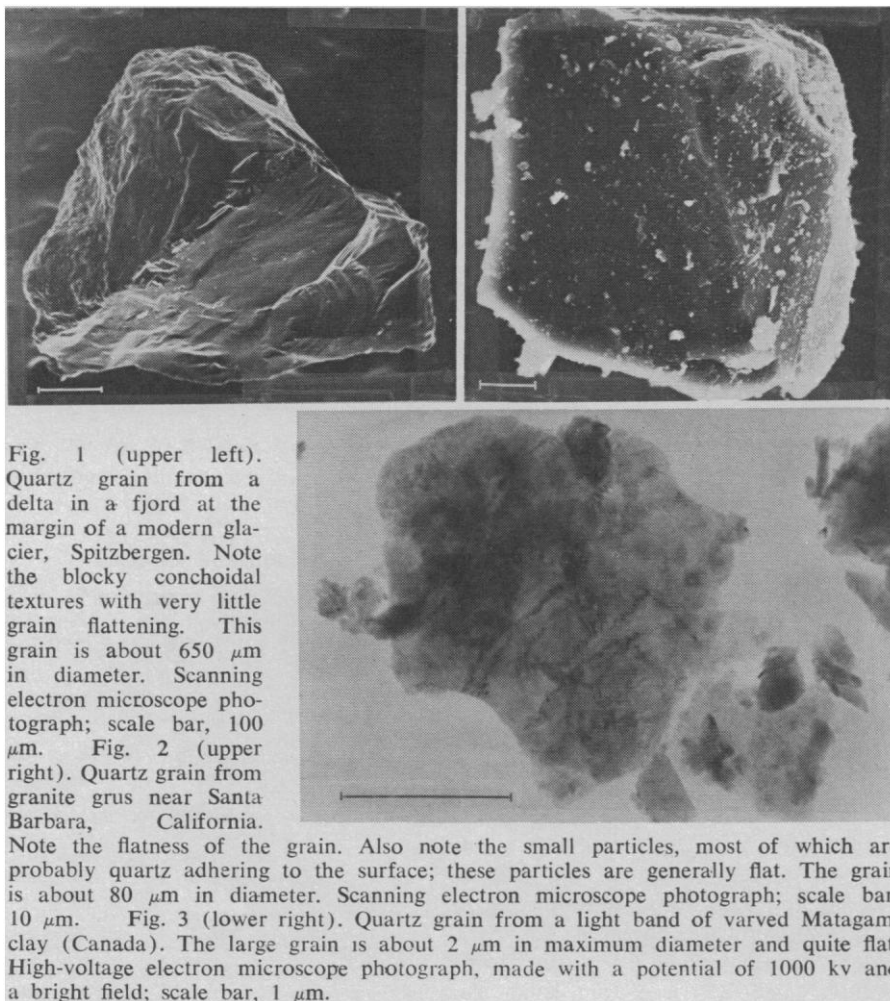


Fig. 1 (upper left). Quartz grain from a delta in a fjord at the margin of a modern glacier, Spitzbergen. Note the blocky conchoidal textures with very little grain flattening. This grain is about 650 μm in diameter. Scanning electron microscope photograph; scale bar, 100 μm . Fig. 2 (upper right). Quartz grain from granite grus near Santa Barbara, California.

Note the flatness of the grain. Also note the small particles, most of which are probably quartz adhering to the surface; these particles are generally flat. The grain is about 80 μm in diameter. Scanning electron microscope photograph; scale bar, 10 μm . Fig. 3 (lower right). Quartz grain from a light band of varved Matagami clay (Canada). The large grain is about 2 μm in maximum diameter and quite flat. High-voltage electron microscope photograph, made with a potential of 1000 kv and a bright field; scale bar, 1 μm .

either silt particles or particles approaching clay size ($< 2 \mu\text{m}$). It is possible that the distribution is the result of a sequential breakage mechanism. The quartz particles are introduced into the sedimentary system initially as sand-sized particles (1) and the first total breakage gives a size reduction of one order of magnitude (for example, from 500 to 50 μm). Total breakage of a 50- μm silt particle gives 5- μm particles, which tend to be classified as clay. Thus, the bulk of sedimentary quartz particles are provided by a breakage sequence: sand (500 to 200 μm) $\rightarrow$ silt (50 to 20 μm) $\rightarrow$ clay size (5 to 2 μm). Examination of silt particles by scanning electron microscopy (SEM) and clay-size particles by high-voltage electron microscopy (HVEM) (2) shows that the particles tend to be flat, and that the flatness increases with decreasing size (Figs. 1 to 3). The probable distribution of particle shapes from purely random breakage gives a predominance of blade shapes (3), but our observations suggest that the actual number of blades (dimension $L_1 > L_2 > L_3$) exceeds the predicted number of blades by

a considerable amount. It is feasible that the "upturned plates" observed on sand grains (4) provide much of the material for clay sediments and that this influences the eventual particle shape.

We propose that the tendency to cleave is suppressed in large quartz

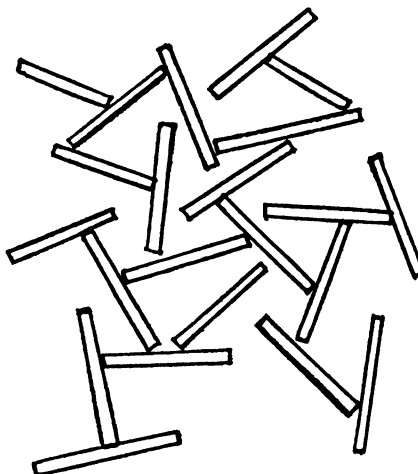


Fig. 4. Idealized sketch of the cardhouse structure once proposed for sediments composed of flat clay mineral particles. [After Moon (6)]

crystals and that less energy is required for failure by fracture. By fracture we mean the separation of a body under stress into two or more portions. Cleavage may be defined as breakage of a body along structurally controlled surfaces, which are parallel to lattice planes and characterized by weak atomic cohesion.

If the fracture mechanism depends on a statistical distribution of defects, then as the particle size is reduced, fracture becomes progressively more difficult. At a certain critical size (assessed as about 100 μm by observation) a crossover occurs, and failure then occurs more easily by cleavage. It has been proposed on the basis of HVEM observations (2) that this cleavage may occur on the (0001) planes (c planes in mineralogical parlance), even though the directions $r(10\bar{1}1)$, $z(01\bar{1}1)$, and $m(10\bar{1}0)$ are believed to be more likely (5).

Certain consequences could follow from the predominance of flat shapes in fine quartz sediments. Recent x-ray diffraction studies (2) have shown that quartz predominates in some postglacial clay soils; if these particles are flat plates (similar in shape to kaolinite) then it may be possible that open structures of the "cardhouse" type do exist in "sensitive" clay soils. A review of data on the structure of clay sediments (6) suggests that very open structures such as the cardhouse structure (Fig. 4) tend not to form in clay mineral sediments, largely because of the nature of the clay mineral particles and their disposition to form domains or packet structures. Thus, despite apparently fundamental differences of opinion, it may be possible to reconcile certain aspects of the debate about quick clay (7); short-range bonds and cardhouse structures may exist. Also, there may be a bearing on the properties of loess deposits; the irregular shapes of the particles could contribute to the openness of their packing and thus be somewhat responsible for the collapsing nature of these soils. Flat particles tend to form a more open packing than spherical particles, and this increases the collapse potential.

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Time Differences in the Formation of Meteorites as Determined from the Ratio of Lead-207 to Lead-206

Abstract. Measurements of the lead isotopic composition and the uranium, thorium, and lead concentrations in meteorites were made in order to obtain more precise radiometric ages of these members of the solar system. The newly determined value of the lead isotopic composition of Canyon Diablo troilite is as follows: $^{206}\text{Pb}/^{204}\text{Pb} = 9.307$, $^{207}\text{Pb}/^{204}\text{Pb} = 10.294$, and $^{208}\text{Pb}/^{204}\text{Pb} = 29.476$. The leads of Angra dos Reis, Sioux County, and Nuevo Laredo achondrites are very radiogenic, the $^{206}\text{Pb}/^{204}\text{Pb}$ values are about 200, and the uranium-thorium-lead systems are nearly concordant. The ages of the meteorites as calculated from a single-stage $^{207}\text{Pb}/^{206}\text{Pb}$ isochron based on the newly determined primordial lead value and the newly reported ^{235}U and ^{238}U decay constants, are 4.528×10^9 years for Sioux County and Nuevo Laredo and 4.555×10^9 years for Angra dos Reis. When calculated with the uranium decay constants used by Patterson, these ages are 4.593×10^9 years and 4.620×10^9 years, respectively, and are therefore 40 to 70×10^6 years older than the 4.55×10^9 years age Patterson reported. The age difference of 27×10^6 years between Angra dos Reis and the other two meteorites is compatible with the difference between the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Angra dos Reis and that of seven basaltic achondrites observed by Papanastassiou and Wasserburg. The time difference is also comparable to that determined by ^{129}I - ^{129}Xe chronology. The ages of ordinary chondrites (H5 and L6) range from 4.52 to 4.57×10^9 years, and, here too, time differences in the formation of the parent bodies or later metamorphic events are indicated. Carbonaceous chondrites (C2 and C3) appear to contain younger lead components.

The absolute ages of meteorites have been determined by $^{207}\text{Pb}/^{206}\text{Pb}$, ^{87}Rb - ^{87}Sr , and ^{40}K - ^{40}Ar methods to be about 4.5×10^9 years. Of these methods, the $^{207}\text{Pb}/^{206}\text{Pb}$ method has an advantage in that it requires only that the isotopic ratio be measured in order that the age of the meteorites be determined, on the assumption either that the initial Pb isotopic composition is known or that some meteorites are cogenetic.

Significant progress has recently been made by Wasserburg and his co-workers (1, 2) in the Rb-Sr chronology of meteorites. Their precise measurements of Sr isotopic ratios and superior mineral separation techniques have effectively confirmed the time difference in meteorite formation which was first found by Reynolds (3) from gas retention ages based on ^{129}Xe derived from extinct ^{129}I . Wasserburg's group obtained many excellent meteorite ages by means of internal isochrons. However, the Rb/Sr ratios are relatively low in most stone meteorites,

especially achondrites; thus only a small change in Sr isotopic composition occurs during the lifetime of meteorites. This has sometimes made Rb-Sr chronology difficult. Furthermore, the decay constant of ^{87}Rb is largely dependent upon the accuracy with which the decay constant of U is known.

Recent precise redeterminations of the decay constants of ^{238}U and ^{235}U (4) and ^{232}Th (5) and of the abundance ratio of ^{238}U to ^{235}U (6) (the values are listed in footnote § of Table 2) and recent improved analytical techniques have encouraged us to carry out the radiometric study presented here of meteorites by the U-Th-Pb system. In the following discussion the reported ages, which were based on old U decay constants, are recalculated on the basis of the new decay constants, and the recalculated values are listed in parentheses for comparison.

Patterson (7) analyzed several meteorites for their Pb isotopic composition and obtained for the first time a pre-

cise age for the meteorites of $4.55 \pm 0.07 \times 10^9$ years (4.49×10^9 years). Because Pb in Pacific sediment fits the Pb array in the meteorites, he concluded that the earth formed contemporaneously with meteorites 4.55×10^9 years ago. Similar data on meteorites obtained later by many scientists (8-10) fell for the most part on an isochron like that which Patterson reported. However, Hamaguchi *et al.* (11) and Bate *et al.* (12) analyzed U and Th concentrations in stony meteorites by neutron activation and reported that the U and Th contents are far lower than those estimated by Patterson to produce the observed Pb isotopic composition and Pb concentration. One might therefore suspect the $^{207}\text{Pb}/^{206}\text{Pb}$ age of meteorites from these results (13). The $^{207}\text{Pb}/^{206}\text{Pb}$ ages of the meteorites obtained in our study range from 4.56 to 4.64×10^9 years (4.50 to 4.57×10^9 years by newly reported U decay constants) which are 10 to 90×10^6 years older than the age that Patterson reported. In this report, instead of discussing the mean age of the formation, we will discuss the time difference in the formation of meteorites which was obtained from the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio.

In the work reported here extensive precautions were taken to avoid possible contamination of samples before and during the analyses. Small (10 to ~ 50 g) specimens of meteorites, except Allende (14), which were free of fusion crust, were washed for 1 minute in cold 2.5N HCl by means of an ultrasonic vibrator and were rinsed repeatedly with water prior to pulverization in a boron carbide mortar. The analytical procedures for silicates reported previously (15) consist of decomposition by HClO_4 -HF in a Teflon bomb and Pb separation by coprecipitation with $\text{Ba}(\text{NO}_3)_2$ and anodic electrodeposition. Troilites were dissolved in a HCl-HNO₃ mixture in a Teflon bomb, and Pb was separated by an anion-exchange (Br^- form resin) technique (16) and anodic electrodeposition; U and Th were separated by an anion-exchange (NO_3^- form resin) method (15). The Pb isotopic ratios were measured by the phosphate-silica gel method (17) in a mass spectrometer equipped with a digital voltmeter and an on-line computer. A correction for the fractionation of $+0.1$ percent per mass unit was applied to the raw ratios. The correction factor was obtained from replicate measurements on standard SRM-982 of the National