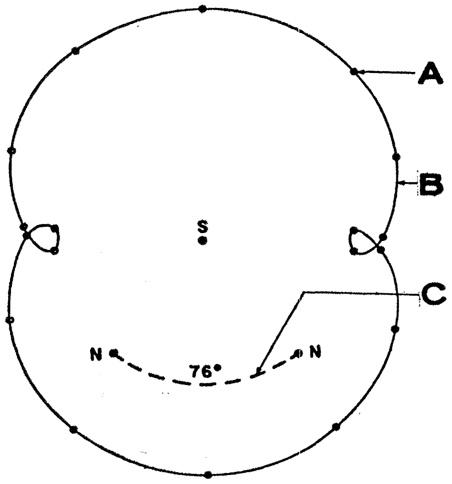

Fig. 1. Path of Pluto about the Sun (S) and Neptune (N) at extrema of libration. (*A*) Solid circles at steps of 10,000 days. (*B*) Synodic period of path, 500 years. (*C*) Period of libration, 20,000 years.

oscillate between 25 and 53 AU and the minimum near the aphelion oscillates from 18 AU at the extrema to almost 22 AU when Neptune is in conjunction at aphelion. The absolute minimum distance between the two planets, 18 AU, is then governed more by the radius of aphelion of Pluto than by the radius of perihelion.

The mechanism of the libration can be appreciated if one considers the attraction of Neptune on Pluto resolved along and transverse to the radius SP from the Sun to Pluto. If this attraction is averaged over a synodic period, the mean radial component can be seen from Fig. 1 to have twice the frequency of the libration. The mean transverse component on the other hand has the frequency of the libration and so must be the cause. At the perihelion loop closer to Neptune, the transverse component is large both because the attraction of Neptune is relatively large and because it makes a large angle with SP. Furthermore, from the solid circles at steps of about 27 years on the path, it is seen that Pluto dwells at each loop for about 25 percent of the synodic period. Thus the transverse attraction of Neptune on the nearer loop dominates the libratory motion. According to whether the nearer loop leads or lags behind Neptune, Pluto loses or gains energy, its mean motion increases or decreases, and in both cases the nearer loop accelerates its librational velocity away from Neptune. In effect, Neptune drives the nearer loop away.

The orbital periods are strictly commensurate at the extrema of the librations. This occurs at just two instants in each libration cycle, and so strict commensurability will almost never be found. This corresponds to the Kirkwood gaps in the asteroids. The amplitude of the libration is governed partly by the initial conditions. If the periods are initially too far from the 3 : 2 commensurability, the acceleration of the loops will not suffice to prevent circulation.

The explanation of the mechanism of the libration is possibly applicable also to asteroids near resonance with Jupiter and to satellites of Jupiter and Saturn (*4*). The number of loops, or incipient loops, though, could be different. There would be three for the 4 : 3 commensurability of the periods of Hyperion-Titan.

In the more analytical language of celestial mechanics, the Pluto-Neptune libration is characterized by an oscillation of the angle $\delta = 3l_P - 2(l_N + \pi_N - \pi_P) - 180^\circ$, where l and π are the mean anomaly and the longitude of perihelion, and P and N are Pluto and Neptune. The period of the libration is about 19,670 years and the amplitude is 76°.

Because of the libration about the commensurability ratio, the closest approach of Pluto to Neptune is locked in near aphelion and the minimum distance between the bodies is approximately 18 AU. Any radical disturbance due to an unusually close approach, which would have to be nearer perihelion, is therefore ruled out.

The libration amplitude is in some error due to the relatively very short span of observations and also is subject to modulation as the orbital elements change. Reasonable secular changes of the elements considerably in excess of those seen in these 120,000 years could hardly break up the libration. Therefore, considering the small radius of perihelion, the orbit of Pluto displays a truly wonderful degree of stability.

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Oxygen Isotope Fractionation between Coexisting Calcite and Dolomite

Abstract. *The oxygen isotopic composition of calcite from carbonate rocks of the lower unit of the Flagstaff formation (Paleocene) exposed along the western margin of the Wasatch Plateau, Utah, is about 7 per mil lower than that of coexisting dolomite, suggesting that isotopic equilibration of these two minerals can occur at relatively low temperatures. Unlike recent isotopic evidence presented by Degens and Epstein, the data do not preclude a primary chemical origin for the dolomite.*

The origin of dolomite, ubiquitous in the rocks comprising the geological record, has been investigated intensively for many decades. Ingerson (*1*), in a recent review of the dolomite problem, stated that the origin and mechanism of formation of the fine-grained, so-called "primary" dolostones remain one of the most interesting and puzzling problems of sedimentary geochemistry. The major problem concerns the question of whether or not dolomite, a stable phase at temperatures and pressures found at the earth's surface (*2*), can crystallize from sea, lake, or river water as a direct chemical precipitate. According to Ingerson, it has never been demonstrated unequivocally that dolomite has ever precipitated in nature directly from solution; nor has dolomite ever been formed in the laboratory under conditions similar to normal marine, lagoonal, or lacustrine environments. To support the arguments for and against the primary origin of at least some dolomite, a wealth of petrographic, stratigraphic, and chemical evidence, all inconclusive, has been

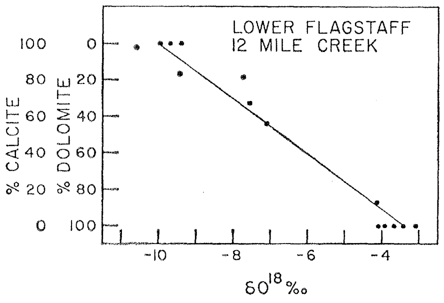

Fig. 1. The O^{18} to O^{16} ratio and the mineralogic composition of carbonate rocks from the lower unit of the Flagstaff formation at 12 Mile Creek Canyon, Central Utah. δO^{18} values are relative to the Chicago PDB standard.

compiled; this evidence has been summarized and reviewed by Fairbridge (*3*).

Recently, a new line of investigation in which O^{18} to O^{16} ratios in dolomites and calcites are used has yielded remarkable results. Epstein *et al.* (*4*) and Clayton and Epstein (*5*) have provided evidence suggesting that dolomite coprecipitated with calcite under equilibrium conditions will differ in δO^{18} by about 8 per mil at 25°C. After oxygen isotopic analysis of a large number of dolomite-calcite pairs from sedimentary carbonate rocks formed in various environments from Cambrian time to the present, Degens and Epstein (*6*) concluded that dolomite is a secondary product resulting from addition of magnesium to preexisting crystalline $CaCO_3$, with the concurrent removal of some calcium. This conclusion was based on the observation that the oxygen isotopic composition of calcite coexisting with dolomite did not significantly differ from the isotopic composition of the dolomite. Therefore, after the calcite was precipitated $CaCO_3$ was transformed to dolomite, without the oxygen isotopes being fractionated; the resulting diagenetic dolomite exhibited the same δO^{18} value as the precursor calcite.

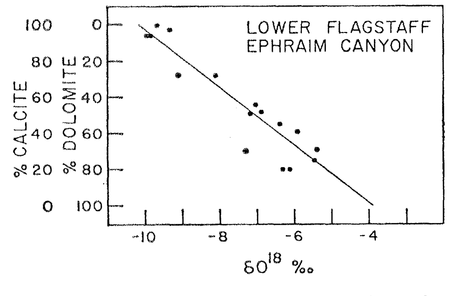

Fig. 2. The O^{18} to O^{16} ratio and the mineralogic composition of carbonate rocks from the lower unit of the Flagstaff formation at Ephraim Canyon, central Utah. δO^{18} values are relative to the Chicago PDB standard.

Carbon and oxygen isotope ratios have been used recently as environmental indicators to interpret the history of Paleocene-Eocene Lake Flagstaff (*7*), the sediments of which are now exposed along the western flank of the Wasatch Plateau in central Utah. Coexisting calcite and dolomite differing in δO^{18} to the extent expected for equilibrium fractionation at 25°C were found. The dolomite-calcite pairs occur in well-defined beds of compact, dense micrite and biomicrite in the lower unit of the Flagstaff formation.

The fine-grained nature of the mineral grains prevents physical separation of dolomite and calcite; other techniques are used to determine the O^{18} to O^{16} ratio of the dolomite and of the calcite from rocks in which the two minerals are intimately intermixed. It should be emphasized that the methods of Degens and Epstein (*6*) differ from those used here.

In the method of Degens and Epstein, carbonate rocks (crushed to −200 mesh) are reacted with 100 percent phosphoric acid under vacuum for 1 hour. The CO_2 thus obtained derives principally from decomposition of calcite. The CO_2 evolved as the reaction proceeds is pumped away and discarded. After 3 hours, further reaction produces CO_2 derived principally from the dolomite. Epstein *et al.* (*4*) justified the procedure in experiments with artifically prepared mixtures of dolomite and calcite of known isotopic composition.

A different technique was used here for the Flagstaff samples. A number of specimens were collected from the lower Flagstaff beds at two localities. By means of x-ray diffraction analyses of the powdered whole rock, the calcite-dolomite ratio was obtained. The percentage of calcite in the rock was determined to within 2 percent by replicate analyses with specially prepared plattens ground to an optical flat (*8*). After heating the powdered sample in flowing helium at 420°C for 20 minutes, about 100 mg of sample was reacted under vacuum with about 10 ml of 100 percent phosphoric acid for 24 hours. The carbon dioxide evolved was purified and analyzed for O^{18} and O^{16} with a 60 degree sector, 6-inch mass spectrometer, with isotopic ratio recording facilities in which the isotopic composition of the sample gas is compared with that of a standard gas every 1.5 minutes under the automatic control of recycling timers. The isotope data are reported in delta notation (δO^{18}) in per mil, relative to the Chicago PDB standard, where

$$\delta O^{18} = 1000 \left(\frac{O^{18}/O^{16}\ \text{sample}}{O^{18}/O^{16}\ \text{standard}} - 1 \right)$$

Total analytical error was less than 0.2 per mil. To determine the isotopic composition of the dolomite and of the calcite, δO^{18} values for the carbonate rock containing calcite and dolomite were plotted against the percentage of calcite in the calcite-dolomite rock. If specimens of pure dolomite were not found, the linear regression line fitted to these points was extrapolated to zero percent calcite.

The results are shown in Figs. 1 and 2. At 12 Mile Creek Canyon (Fig. 1), the lower beds of the Flagstaff formation vary in composition from pure dolomite to pure calcite. Calcite, about −10 per mil, is approximately 7 per mil lighter ($\delta O_{dol}^{18} - \delta O_{ct}^{18} = 7$) than dolomite from the same stratum. Samples collected from Ephraim Canyon (Fig. 2), from the same stratigraphic horizon, do not include specimens of pure dolomite. The δO^{18} value for dolomite has been determined by extrapolation of the linear regression line to zero percent calcite, yielding an isotopic composition of about −4 per mil. In this case, fractionation of oxygen isotopes between coexisting calcite and dolomite is about 6 per mil.

In each case, the difference between δ_{ct} and δ_{dol} is close to the value of 8 per mil expected at room temperature, suggesting that oxygen isotopic equilibration has taken place between calcite and dolomite at temperatures found at the earth's surface. It should be emphasized that the Flagstaff carbonates analyzed are dense, compact, and in some cases sublithographic dolomitic limestones which have never been deeply buried. Although it has not been proved that post-depositional isotopic exchange of calcite with O^{16}-enriched ground water has not taken place, the lithologic characteristics of these carbonates make this event unlikely. The sediments are early Tertiary in age, and no traces of larger, euhedral dolomite rhombs, usually ascribed to diagenetic replacement of calcite, were evident in thin-section. Furthermore, all weathered surfaces were removed before analysis, and considerable care was taken to ensure that only fresh material was used. The fact that the oxygen isotopic compositions of the dolomite and calcite differ by the expected amount, and in the correct direction, does not prove that dolomite is a primary chemical precipitate, nor does it exclude this possibility as the data presented by Degens and Epstein do. The Flagstaff data do suggest, however, that isotopic equilibration between calcite and dolomite can occur at relatively low temperatures. Whether equilibration occurs when calcite and dolomite are coprecipitated, or later by penecontemporaneous dolomitization of unconsolidated sediments, remains an unanswered question.

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Mononuclear and Polynuclear Chemistry of Rhenium (III): Its Pronounced Homophilicity

Abstract. *Extensive chemical, spectrophotometric, and x-ray structural studies have shown that trivalent rhenium is strongly homophilic—that is, it tends to form bonds to other* Re^{III} *atoms—and it forms at least three different series of* $[ReX_4]_n^{n-}$ *complexes. The mononuclear, square complex,* $[ReBr_4]^-$*, adds two water molecules to give* trans-$[ReBr_4(H_2O)_2]^-$*. The binuclear complexes* $[Re_2Cl_8]^{2-}$ *and* $[Re_2Br_8]^{2-}$ *have strong Re-Re bonds, unsupported by halide bridges. The trinuclear species,* $[Re_3X_{12}]^{3-}$ *or* $Re_3X_9L_3$*, contain the triangular* Re_3X_9 *clusters. Use of* $ReCl_3$ *appears always to lead directly to products containing* Re_3Cl_9*; this unit exists in* $ReCl_3$ *itself and does not appear to be kinetically labile. The* $[Re_2X_8]^{2-}$ *ions are obtained by reduction of* ReO_4^- *in aqueous HCl or HBr. Salts of* $[ReBr_4(H_2O)_2]^-$ *can be obtained directly from solutions of* $ReBr_3$ *in HBr along with numerous other compounds, some containing trinuclear clusters.*

A tendency for an atom to form bonds to one or more others of the same chemical identity may be termed homophilicity (*1*). While it is a pronounced property of many nontransition elements, it is much less common among transition elements. It appears to be favored by lower formal oxidation numbers (becoming quite pronounced for oxidation number zero) and higher atomic numbers. Among compounds exemplifying homophilicity (*2*) are the newly discovered trinuclear cluster compounds of rhenium(III) (*3–5*). The chemistry of rhenium(III) has now been investigated more comprehensively, the initial purpose being determination of the generality of occurrence of trinuclear clusters. The actual result has been the discovery that rhenium(III) forms at least three series of complexes, mono-, bi-, and trinuclear.

The parent compound for all known trinuclear chloro complexes is $ReCl_3$, which itself contains trinuclear clusters (*6*). It crystallizes in the space group $R\bar{3}m$, with 18 formula units per hexagonal cell. The six trinuclear clusters lie on the *6c* positions and have *3m* (C_{3v}) symmetry. All of the internal dimensions of the Re_3Cl_9 unit in crystalline $ReCl_3$ are approximately the same as corresponding dimensions in $[Re_3Cl_{12}]^{3-}$, $[Re_3Cl_{11}]^{2-}$, and $Re_3Cl_9(PEt_2Ph)_3$, at a stage of refinement of the $ReCl_3$ structure where the conventional residual stands at 16 percent.

All compounds of Re^{III} that we have prepared from $ReCl_3$, as well as all nonaqueous solutions of $ReCl_3$ and solutions in aqueous HCl, exhibit only the absorption bands in the near infrared, visible, and near ultraviolet, which we consider (*5*) to be characteristic of the Re_3Cl_9 cluster. It thus appears that this cluster is very stable—kinetically, at least, and perhaps also thermodynamically—and that it therefore forms a basis for "one of the chemistries" of trivalent rhenium.

In the Re^{III}-Br system, the analogous Re_3Br_9 cluster also is of some importance. The red-black $Re_3Br_9(PEt_2Ph)_3$ is isomorphous with $Re_3Cl_9(PEt_2Ph)_3$, and these two compounds have quite similar electronic absorption spectra. The compound $ReBr_3$ has not yet been obtained in crystals suitable for complete structure determination, but powder x-ray data suggest that the structure may be quite similar to that of $ReCl_3$, and solutions in both aqueous HBr and nonaqueous solvents exhibit spectra showing the presence of Re_3Br_9 clusters, though not exclusively. The structure of the clusters is such that internal strains caused by repulsion of nonbonded halogen atoms could perhaps become severe enough in the bromine case to labilize or destabilize (or both) the trinuclear structure relative to simpler ones.

A "second chemistry" of trivalent rhenium has for its chief structural feature binuclear species which have very short and strong Re-Re bonds without any halogen bridges. The simplest members of this class are the various salts of $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$, with cations, such as K^+, NH_4^+, and quaternary ammonium, phosphonium, and arsonium ions. These may be prepared by reductions of solutions of ReO_4^- in aqueous HCl or HBr with hypophosphite ion. Yields are quite sensitive to reaction conditions, varying from essentially zero under many circumstances to around 20 percent under optimum conditions. The $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions can be interconverted simply by heating the former in aqueous HBr and the latter in aqueous HCl. These compounds are actually the same types as, in some cases identical with, a series reported by Russian workers (*7*), but in our view the compounds were incorrectly identified and formulated by them (*8*) as Re^{II} complexes.

The compound $K_2Re_2Cl_8 \cdot 2H_2O$ crystallizes in the space group $P\bar{1}$ and contains one formula weight per unit cell. The $[Re_2Cl_8]^{2-}$ anion, which is required by the space group to be centric, has approximately D_{4h} symmetry. Some of its principal dimensions are shown in Fig. 1. The Re-Re distance (2.24 Å) is to be compared with that (2.48_5 Å) in the Re_3Cl_9 cluster (*2, 4, 5*). The water molecules are coordinated to the K^+ ions and not to the rhenium atoms.

The fact that $[Re_2Cl_8]^{2-}$ has an