andalusite, in agreement with the results of other workers.

The triple points resulting from the squeezer determinations lie well outside the present limits of error. A determination calculated from heat of solution measurements in a fused-salt calorimeter by Holm and Kleppa (*12*) lies somewhat closer to my result. The triple point calculated by Weill (*13*) from measurements of the solubilities of the aluminum silicates in fused cryolite at 1 atm borders on the present limits of error. The water-solubility data (*14*) bearing on the relative stability of the polymorphs at 700°C and 3 kb is also consistent. The point on the andalusite-sillimanite boundary deduced by Evans (*15*) from the apparent positions of the reactions of muscovite and quartz to yield potash feldspar and sillimanite or andalusite lies between 600° and 640°C at about 2½ kb.

The discrepancy between the present results and the squeezer determinations cannot be accounted for by pressure uncertainty in the present runs, presence of Fe_2O_3 in the system, formation of alternative phases, or strain or orientation effects on the peak height of the x-ray signal. If water preferentially entering the kyanite structure causes the discrepancy, then my experiments establish that availability of water produces the same variation of *P-T* stability in nature, for the kyanite formed from well-crystallized natural andalusite and vice-versa over a small pressure interval of uncertainty. That the possibility of the formation of water-bearing kyanite is small is indicated by the normal *d*-spacings of overgrowths from runs showing complete reaction, the small interval of uncertainty adjacent to the kyanite-andalusite boundary, and the fact that normal, water-free kyanite is often found as hydrothermal vein deposits in metamorphic rocks.

The heats of formation of the Al_2SiO_5 polymorphs calculated by Waldbaum (*16*) were based on the triple-point locations of Khitarov *et al.* (*2*) and Bell (*3*), and hence may require some revision.

Figure 2 implies that andalusite-bearing rocks form at depths no greater than 12 to 15 km. The corresponding temperatures can be progressively higher as depth of origin is decreased. Kyanite is known to have inverted to andalusite in the thermal aureoles around some granite bodies (*17*), and to sillimanite in others (*18*). If this represents equilibrium inversion, the granite was emplaced at a depth less than 15 km in the former case and at greater depth in the latter. The conditions for the classical sillimanite "isograd" are 4 to 6 kb and 500° to 600°C, according to Fig. 2.

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2 May 1966

Thermal Conductivity Effect of Carrier Gases on Flame-Ionization Detector Sensitivity

Abstract. *Data for six carrier gases of different thermal conductivities show a linear correlation between the logarithm of thermal conductivity and detector response. Carbon dioxide with a lower thermal conductivity than helium gives a ninefold increase in detector response.*

When other variables are held constant, the sensitivity of a flame-ionization detector is a direct function of flame temperature (*1*). Optimum ion yield results from flames of highest possible temperature that give maximum detector response (*2*). Ionization efficiency and flame-ionization detector response are greatly reduced with carrier gases of high thermal conductivity because these tend to decrease flame temperature.

Figure 1 relates sensitivity of the flame-ionization detector, as measured by peak height, to isothermal column temperature for six carrier gases of different thermal conductivities. Peak height is maximum when temperatures of the column are highest; however, triangulated peak areas are kept constant by sample injections of equal size. All operating parameters were held constant. In a comparison of the usual carrier gas, He, with CO_2, it is clearly evident that CO_2 offers greatest flame-ionization-detector sensitivity over the experimental temperature ranges used. At a column temperature of 100°C, peak heights with CO_2 were about nine times greater than those recorded with He as the carrier gas. Other carriers exhibited peak heights in agreement with their thermal conductivities and with those observed for CO_2 and He. Figure 2 shows that flame-ionization detector response depends logarithmically upon the thermal conductivities of the carrier gas and illustrates the advantages of carriers of low thermal conductivity.

When maximum sensitivity of the flame ionization detector is desired, a carrier gas with the lowest possible thermal conductivity, in keeping with good column efficiency, should be chosen. Maximum column efficiency in gas-solid chromatography may not always be provided by carriers of low thermal conductivity because of the competition between carrier and sample for active sites on the adsorbent (*3*). In gas-liquid chromatography, column efficiency is not so powerfully influenced by the carrier gas employed.

For the operator's convenience, many chromatographic instruments equipped with both flame-ionization and thermal conductivity detectors are often plumbed to use only He because it is required by the thermal-conductivity detector for maximum sensitivity. Although hydrogen gives slightly greater sensitivity for thermal-conductivity detection, its explosive properties make it an infrequent choice. Furthermore, little advantage can be gained in sensitivity through use of H_2 as a carrier gas since its thermal conductivity is 41.6×10^5 cal cm^{-1} sec^{-1} $(°C)^{-1}$, compared with 34.8×10^5 for He—a unit increase of only 9 percent. Installation of a manifold for operation of the column with either N_2, or CO_2 when feasible, for the flame-ionization

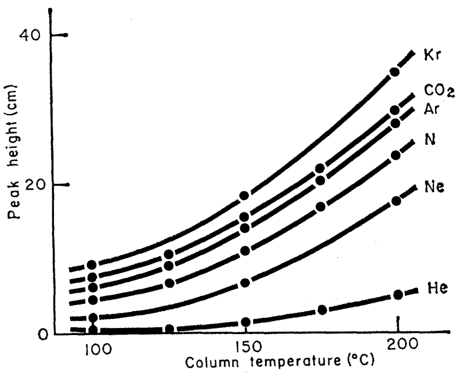

Fig. 1. Peak-height sensitivity plotted against column temperature, showing the effect of carrier-gas thermal conductivity on the response of the flame ionization detector. Column, 122 cm by 0.3 cm; activated alumina. Sample, *n*-butane (gas). All instrumental parameters held constant. The thermal conductivities [10^5 cal cm^{-1} sec^{-1} $(°C)^{-1}$] at 0°C are Kr, 2.0; CO_2, 3.5; Ar, 4.0; N, 5.8; Ne, 10.9; and He, 34.8.

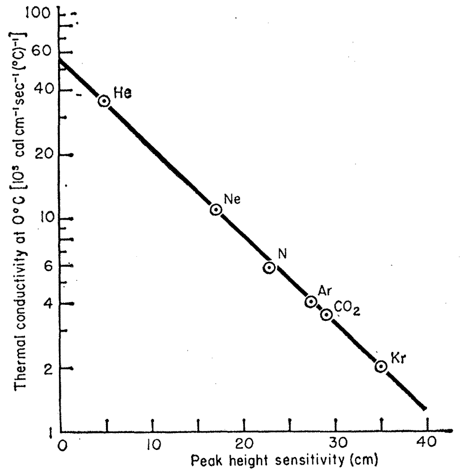

Fig. 2. Peak-height sensitivity plotted against logarithm of carrier-gas thermal conductivity for a column, operated isothermally at 200°C.

detector and with He for the thermal-conductivity detector provides more versatile equipment and allows operation of each detector at its maximum sensitivity.

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Oxygen Isotope Studies of Ivory Coast Tektites and Impactite Glass from the Bosumtwi Crater, Ghana

Abstract. *Oxygen isotope analyses were obtained for six Ivory Coast tektites, two samples of Bosumtwi Crater glass, and two new moldavites. The Ivory Coast tektites are 2 to 5 per mil richer in oxygen-18 than other known tektites, and they are similar in oxygen-18 content to the impactite glass from the nearby Bosumtwi Crater. These data are compatible with a terrestrial origin for the Ivory Coast tektites.*

The ratios of O^{18} to O^{16} of six Ivory Coast tektite specimens are appreciably different from those of other known tektites. Values are given in Table 1 in the familiar δ-notation:

$$\int = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right] 1000$$

where R_{standard} is the ratio of O^{18} to O^{16} of standard mean ocean water. The δ-values of Ivory Coast tektites are 12.8 to 14.6 per mil higher than the ocean-water mean, making them 2 to 5 per mil richer in O^{18} than other tektites (*1*, *2*). These data raise the question of whether the Ivory Coast tektites have the same origin as the other tektite-strewn fields; the latter are much larger in area than the Ivory Coast field, and they are more uniform in O^{18} content.

Included in Table 1 are oxygen isotope analyses of two impactite glasses from the Bosumtwi Crater in Ghana. This crater has been suggested by Cohen (*3*) as the site of ejection of the Ivory Coast tektites, presumably by shock melting during the meteorite impact associated with the origin of the Bosumtwi Crater (*4*). Geochemical data now support such an hypothesis. The K-Ar age determinations of Ivory Coast tektites (*5*) and of Bosumtwi Crater glass (*6*) are identical within experimental error at 1.3×10^6 years; this value is also supported by fission-track dating (*7*) as indicating the time of melting of the impactite glass and the Ivory Coast tektites. Schnetzler *et al.* (*8*) and Lippolt and Wasserburg (*9*) have also shown that these tektites, the crater glass, and the igneous and metamorphic rocks exposed in the area of the Bosumtwi Crater all lie on the same Rb-Sr isochron, suggesting that they were derived from rocks with an age of about 2.0×10^9 years. Many chemical similarities also have been found between Ivory Coast tektites and Bosumtwi Crater glass (*6*, *8*).

The impactite glass samples from Bosumtwi Crater show a range of δO^{18} (12.0 to 14.8) that is practically identical to the range of O^{18} in Ivory Coast tektites (12.8 to 14.6), although only two samples of the impactite glass have been analyzed. The variations of O^{18}/O^{16} in the glass could be reasonably attributed to variations in the parent rock types exposed in the Bosumtwi Crater area, although none of these has been analyzed. The δ-values obtained are typical for gneisses and metamorphosed sedimentary rocks (*1*, *10*, *11*); the δ-value of 14.8, in particular, is representative of the argillaceous sedimentary and metasedimentary rocks. Some of the variation in O^{18} content of the glass could be a result of the impact process itself, as oxygen isotope changes generally take place in rocks during melting and dehydration (*2*).

Two new analyses of tektites from the moldavite-strewn field also were made, and are included in Table 1. With these results, we now have a statistically significant amount of data from the four known tektite-strewn fields. The principal features of the existing oxygen isotope data on tektites and impactite glasses (Fig. 1) are (i) the great similarity in the ratios of O^{18} to O^{16} in tektites from the three major strewn fields in Australasia, North America, and Czechoslovakia; (ii) the marked difference between the Ivory Coast tektites and the other types; (iii) the great variability of O^{18}/O^{16} in the impactite glasses, whose ratios range from 7.9 to 14.8 and hence cover most of the range (7 to 19 per mil) shown by the common rocks rich in SiO_2 (excluding cherts) exposed at the Earth's surface; and (iv) the similarity of O^{18}/O^{16} in the Bosumtwi Crater glass and the Ivory Coast tektites.

The Ivory Coast tektites appear to be true tektites in terms of their internal structures, major element chemical composition, and external morphology (*12*); they have, however, slightly lower SiO_2 contents (and higher indices of refraction) than the other tektites. The only known features which clearly distinguish the Ivory Coast tektites from other tektites are their ratios O^{18}/O^{16} and Rb/Sr. A rough isochron, 400×10^6 year, can be drawn through the average values of Rb^{87}/Sr^{86} and $Sr^{87}/$