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THERMOPHYSICAL PROPERTIES OF OIL SHALE MINERALS

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ABSTRACT

The thermal diffusivity values of eight minerals that are commonly associated with oil shales of the Green River formation have been measured by the laser flash technique. Data are presented in the temperature range 25–500 °C for quartz, dolomite, calcite, plagioclase, analcite, pyrite, potassium feldspar and low albite. A comparison of the thermal conductivities of some of these minerals, calculated from experimentally measured thermal diffusivity and density, with the experimental values reported in the literature reveals good agreement. Trends in the variation of thermal diffusivity with temperature and anisotropic effects in thermophysical parameters are discussed from the point of view of grain boundary effects in these polycrystalline mineral aggregates.

INTRODUCTION

Thermal diffusivity determines the temperature–time history in a material for a given set of boundary conditions; it is a critical parameter for the diffusion of heat under various thermal excitation schemes[1]. Furthermore, a knowledge of this parameter enables calculation of another useful thermophysical property, namely, the thermal conductivity, through the equation

$$\alpha = \kappa/\rho c \tag{1}$$

where α is the thermal diffusivity, κ the thermal conductivity, ρ the density and c the specific heat of the material.

In a previous paper[2], we reported on the measurement of the thermal diffusivity of Green River oil shales with oil yield and temperature as the variable parameters. A complete characterization of the thermophysical behavior of Green River oil shales, however, necessitates a knowledge of the thermal behavior of their constituent minerals. In this regard, Green River oil shales represent virtually a "mineral storehouse"; a large number of minerals has been discovered and characterized in the shales

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TABLE 1

ORIGIN AND CHEMICAL ANALYSES OF MINERAL SAMPLES

Mineral	*Location*	*Chemical analysis*[a] *(wt. %)*								
		Na	*K*	*Ca*	*Mg*	*Si*	*Al*	*Fe*	H_2O	*Ash*
Analcite ($NaAlSi_2O_6 \cdot H_2O$)	Italy	9.7			<0.1	23.6	10.5	<0.1	9.9	90.1
Pyrite (FeS_2)	Gillman, Colorado							ND[b]		
Quartz (SiO_2)	Larimer County, Colorado		0.1			46.8		<0.1		100.0
Dolomite ($CaMg(CO_3)_2$)	Larimer County, Colorado		<0.1	23.8	14.3	<1	<1			61.1
Calcite ($CaCO_3$)	Chihuahua, Mexico			40.5		<1	<1			59.0
Potassium feldspar ($KAlSi_3O_8$)	West Maroon Pass, Colorado	2.1	11.2		<0.1	29.3	10.2	0.2		
Albite ($NaAlSi_3O_8$)	Larimer County, Colorado	ND					ND			
Plagioclase-1		8.4	1.8	<0.2	<0.1	32.6	10.3	<0.1	0.11	
Plagioclase-2	Larimer County, Colorado	8.9	0.8	<0.2	<0.1	30.3	10.1	<0.1	0.10	
Plagioclase-3 ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$)		3.1	10.2	<0.2	<0.1	30.3	9.6	<0.1	0.12	

[a] Elemental analyses by atomic absorption spectroscopy; water and ash by gravimetric methods.
[b] Not determined.

of the Green River formation[3]. Some of these such as nahcolite and dawsonite are of considerable importance for the generation of valuable by-products during processing of oil shale[4]. The manner in which these minerals are modified by combination with the indigenous organic matter will determine the overall thermophysical behavior of oil shale.

Accordingly, an investigation was undertaken to characterize the thermophysical properties of minerals commonly associated with Green River oil shales. The results of thermoanalytical studies such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) on most of these minerals have been reported in the literature[3]. Literature data on the thermal conductivities and thermal diffusivities on the other hand are fragmentary; the data on the few minerals that have been reported are limited to a narrow temperature range and are also incomplete in most cases. This paper reports on the thermophysical parameters of eight minerals present in the shales of the Green River formation.

EXPERIMENTAL

Technique

The thermal diffusivities were measured by the laser-flash technique[5,6]. Details of the experimental arrangement and calibration are reported elsewhere[2].

Samples

Samples of quartz, dolomite, calcite, plagioclase, analcite, pyrite, potassium feldspar and low albite were obtained in naturally-occurring form from commercial sources. The location and chemical analyses of these samples are listed in Table 1. Right-circular cylindrical cores, 12.5 mm diameter, 2 mm thick, were cut from massive blocks of the minerals for diffusivity measurements. Reproducibility of the experimental results and any possible variations arising from sample to sample compositional differences were systematically checked by coring duplicate samples at $\sim$ 10 cm intervals from the same block. Anisotropic effects were investigated by coring samples in different directions* with respect to the orientation of the massive blocks. All samples were carefully dried to remove free moisture and then stored in a vacuum desiccator prior to measurements.

Data analysis

Standard statistical and computer techniques were employed to derive exponential and quadratic equations relating the experimentally determined thermal diffusivity values to the variable parameter, namely temperature. Statistical methods using regression analysis were used to fit experimental data to curves showing the variation of thermal diffusivity with temperature for the different minerals examined in the present study.

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* The absence of sedimentary varves (unlike in the case of oil shale) and definite crystallographic planes in the polycrystalline mineral samples makes the choice of these directions somewhat arbitrary.

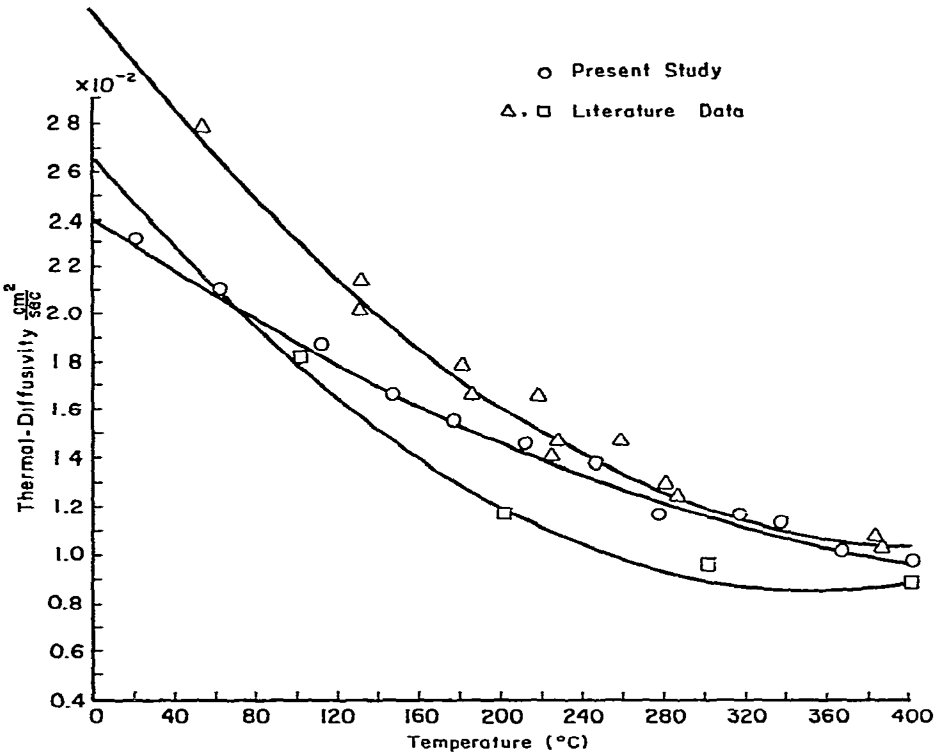

Fig. 1. Variation of thermal diffusivity with temperature for polycrystalline quartz. Literature data taken from Touloukian et al.[7].

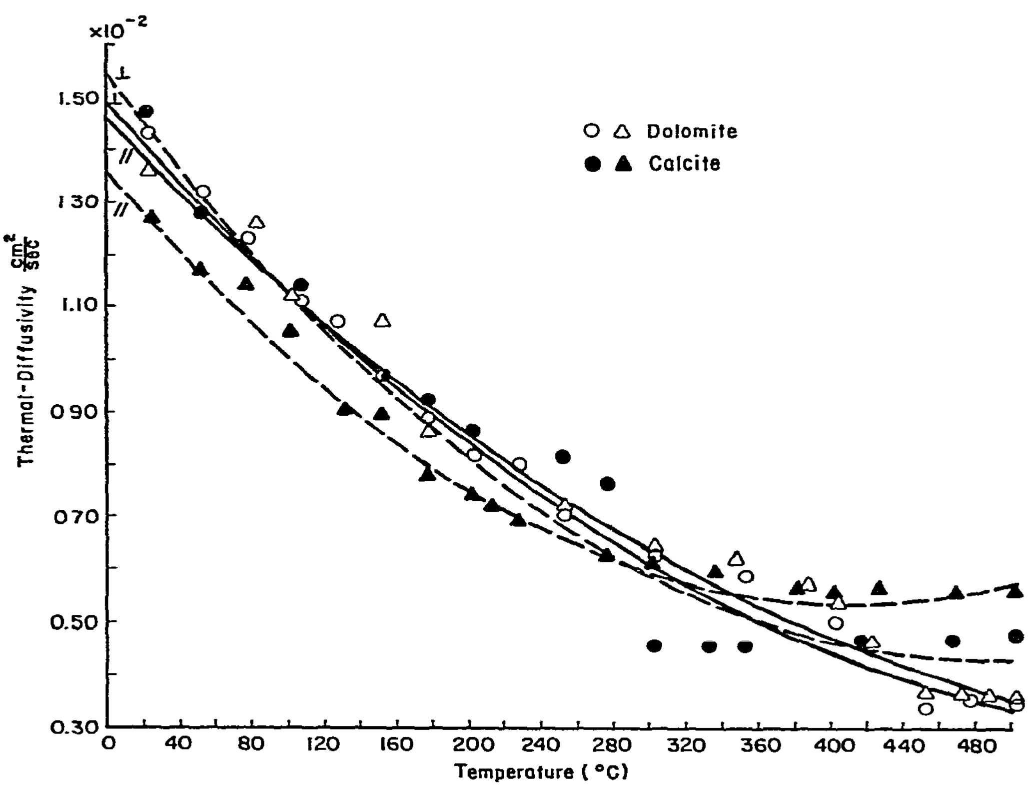

Fig. 2. Thermal diffusivity–temperature relationships for polycrystalline dolomite and calcite samples ($\perp$ = samples cut perpendicular to coring planes; $\|$ = samples cored in a parallel orientation).

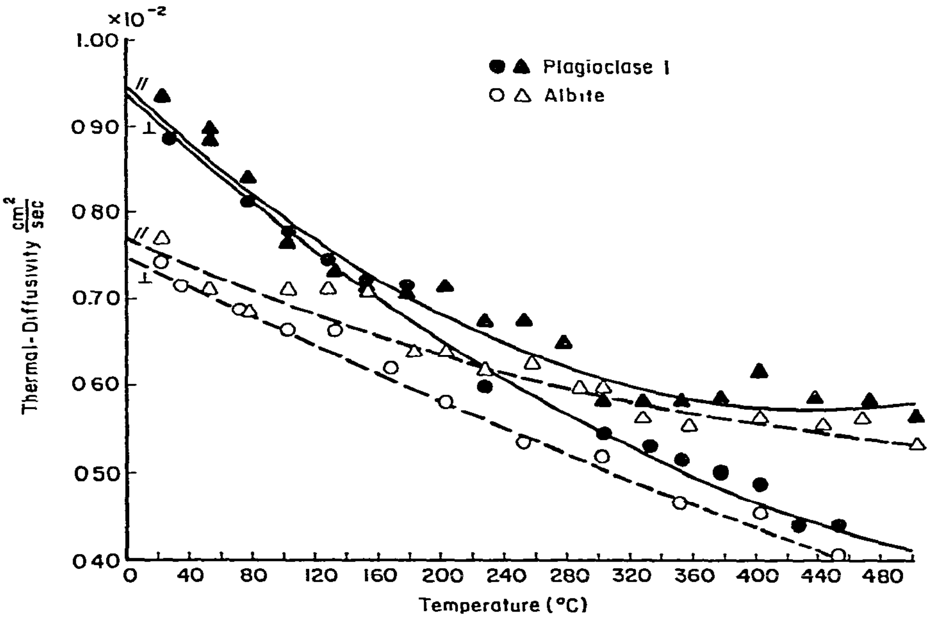

Fig. 3. Variation of thermal diffusivity–temperature for low albite and plagioclase-1.

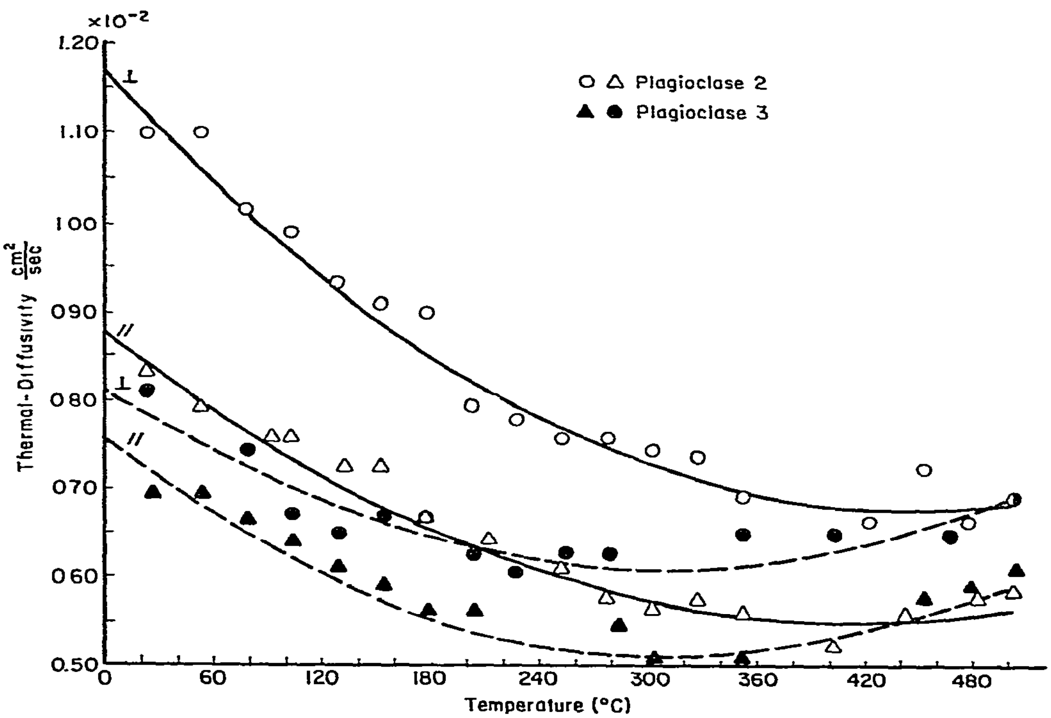

Fig. 4. Thermal diffusivity–temperature variation for plagioclase-2 and plagioclase-3.

RESULTS

Figure 1 shows typical results obtained in the present study on polycrystalline quartz samples. Trends in the variation of the thermal diffusivity with temperature

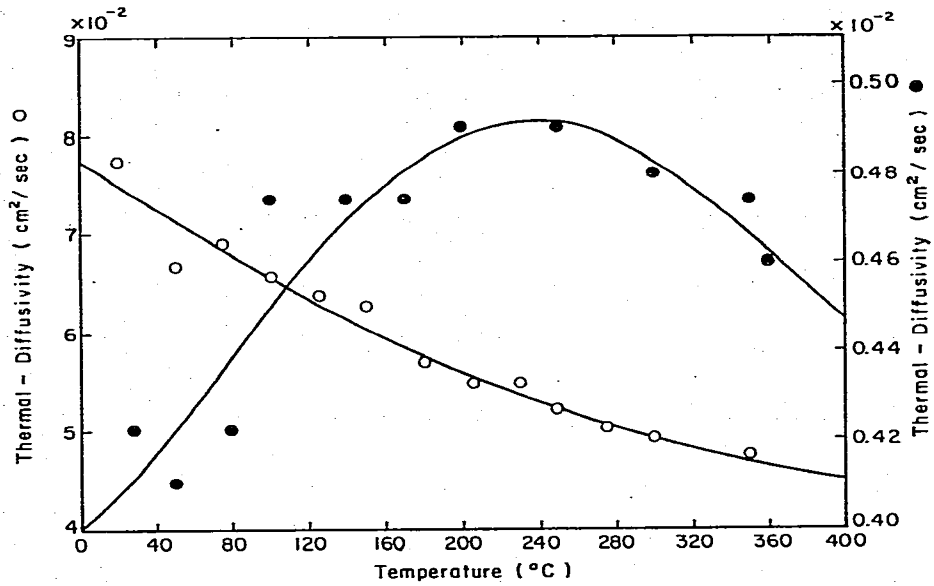

Fig. 5. Variation of thermal diffusivity with temperature for pyrite (O) and analcite (●).

for this material are compared with results in the literature[7, 8]. Agreement with published results is seen to be excellent, especially when one takes into account differences in the location and dispositional history of these samples.

Figure 2 shows the corresponding results for dolomite and calcite. Data is presented for samples cored in two different directions with respect to the massive blocks. Anisotropic effects in the thermal diffusivity values are seen to be relatively small.

Figures 3 and 4 present results on low albite and three different types of plagioclase (labeled plagioclase-1, -2 and -3, respectively). Anisotropic effects are small for albite and plagioclase-1 (except at high temperatures $< 300\,°C$) whereas they are significantly large for plagioclase-2 and -3 (Fig. 4).

Figure 5 shows the variation of thermal diffusivity with temperature for pyrite. No anisotropic effects were observed for this material.

A statistical analysis of the trends in the experimental results for the above minerals yields the following predictive second-order equation which relates the thermal diffusivity (α) to temperature (T)

$$\alpha = a + bT + cT^2 \tag{2}$$

where a, b and c are constants. These coefficients are listed for the various minerals in Tables 2 and 3.

Interesting effects in the variation of thermal diffusivity with temperature were observed for analcite and potassium feldspar. The data for these minerals are shown in Figs. 5 and 6, respectively. The thermal diffusivity values for potassium feldspar are also seen to show considerable anisotropy (Fig. 6), the values differing by $\sim 30\%$ depending on the direction of heat flow with respect to the orientation of the coring planes.

TABLE 2

COEFFICIENTS IN THE EQUATION $\alpha = a + bT + cT^2 + dT^3$ FOR MINERALS WITH INSIGNIFICANT ANISOTROPIC EFFECTS

Mineral	*a*	*b*	*c*	*d*
Dolomite	1.48	-3.84×10^{-3}	3.10×10^{-6}	0
Calcite	1.54	-4.63×10^{-3}	4.79×10^{-6}	0
Albite	0.93	-1.41×10^{-3}	1.13×10^{-6}	0
Quartz	2.40	-5.88×10^{-3}	5.70×10^{-6}	0
Analcite	0.14	3.33×10^{-4}	3.22×10^{-6}	-2.00×10^{-8}
Plagioclase-1	0.94	-1.68×10^{-3}	1.26×10^{-6}	0
Pyrite	8.62	-1.45×10^{-2}	5.33×10^{-6}	0

TABLE 3

COEFFICIENTS IN THE EQUATION $\alpha = a + bT + cT^2 + dT^3 + eT^4$ FOR MINERALS WITH STRONG ANISOTROPIC EFFECTS

Mineral		*a*	*b*	*c*	*d*	*e*
Plagioclase-2	$\perp$[a]	1.17	-2.22×10^{-3}	2.50×10^{-6}	0	0
	$\parallel$	0.88	-1.57×10^{-3}	1.91×10^{-6}	0	0
Plagioclase-3	$\perp$	0.75	-1.53×10^{-3}	2.42×10^{-6}	0	0
	$\parallel$	0.81	-1.29×10^{-3}	2.12×10^{-6}	0	0
Potassium feldspar	$\perp$	0.46	-4.71×10^{-2}	0.70×10^{-4}	-0.32×10^{-6}	5.0×10^{-10}
	$\parallel$	0.81	-0.81×10^{-2}	1.04×10^{-4}	-0.48×10^{-6}	7.0×10^{-10}

[a] $\perp$ and $\parallel$ refer to perpendicular and parallel orientations of coring planes with respect to direction of heat flow.

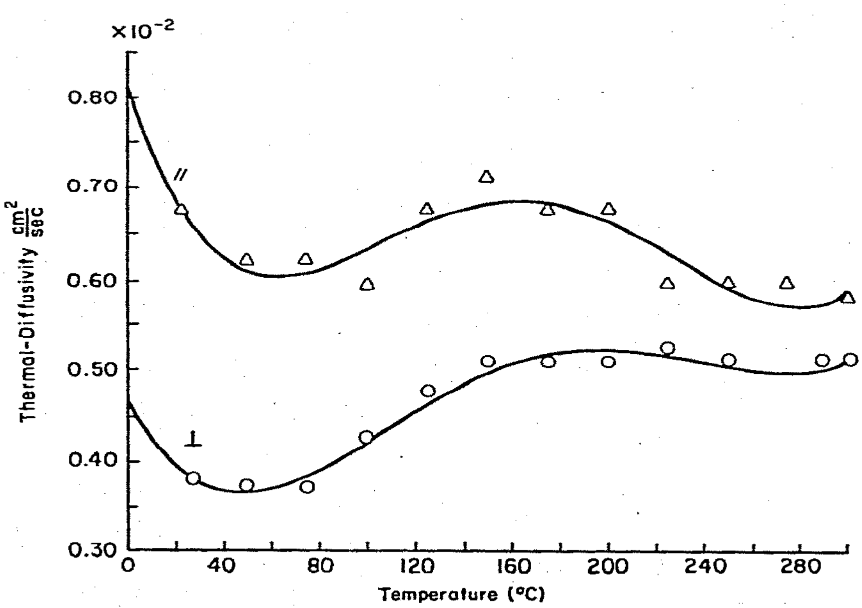

Fig. 6. Variation of thermal diffusivity with temperature for potassium feldspar.

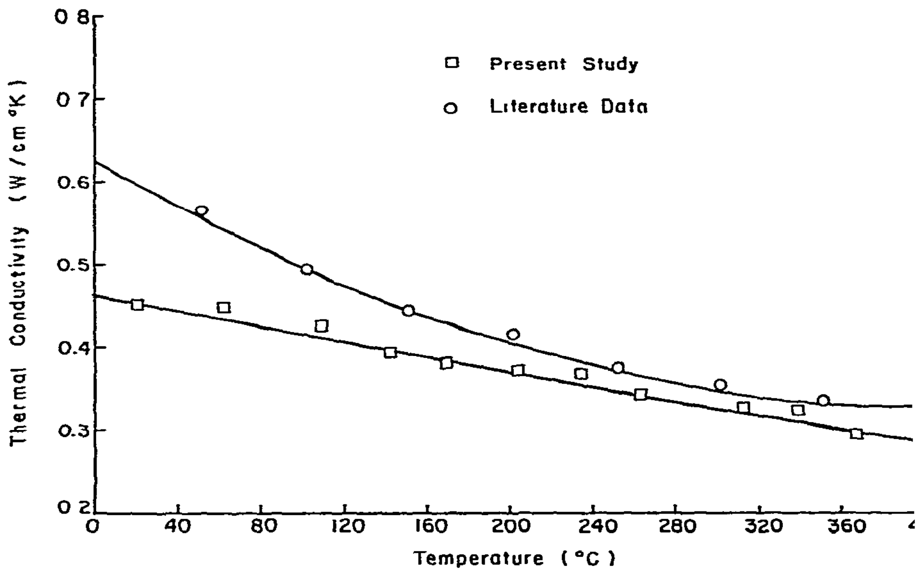

Fig. 7. Variation of thermal conductivity (calculated from experimental temperature for polycrystalline quartz. Literature data taken from Toulouki

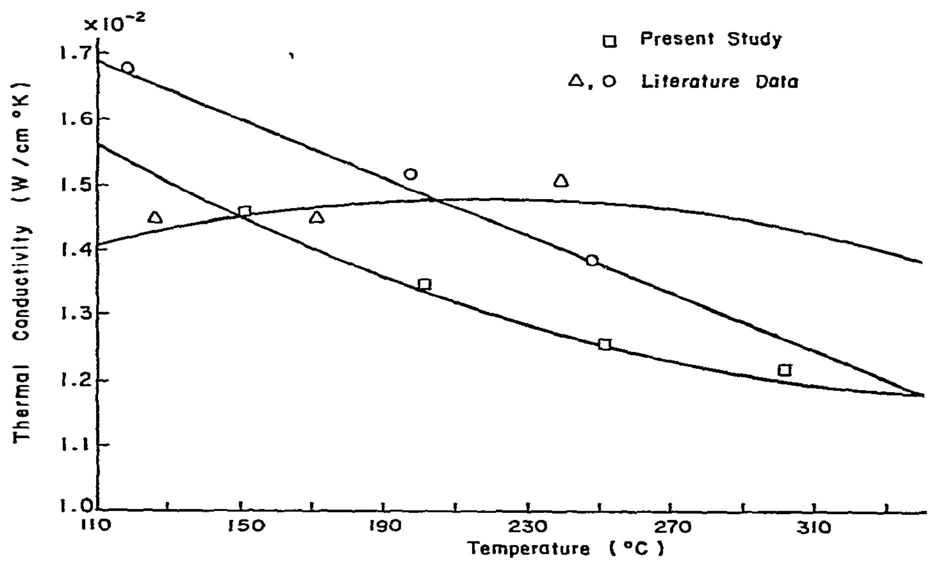

Fig. 8. Thermal conductivity–temperature variation for polycrystalline calcite from Touloukian et al.[7].

The above data for analcite and potassium feldspar were fourth-order equations, respectively.

$$\alpha = a + bT + cT^2 + dT^3$$

and

$$\alpha = a + bT + cT^2 + dT^3 + eT^4$$

The coefficients in equations (3) and (4) are listed in Tables 2 an

TABLE 4

THERMAL CONDUCTIVITY OF MINERALS (25 °C) CALCULATED FROM THEIR THERMAL DIFFISIVITY AS COMPARED WITH EXPERIMENTALLY DETERMINED VALUES

Mineral	*Thermal conductivity (10^{-2} W cm^{-1} °C^{-1})*		*Ref.*
	Present study	*Lit.*	
Dolomite	3.29–3.46	4.31	15
Analcite	0.98	1.26	17
Albite	2.08	2.35	17
Pyrite	20.56	19.22	17
		37.93[a]	15

[a] Single crystals.

Thermal conductivity values for some of the minerals listed in Table 1 were calculated from experimentally measured thermal diffusivity and density through use of eqn. (1). The corresponding heat capacity data for these minerals were obtained from the literature[8-13]. Figures 7 and 8 show the thermal conductivity of quartz and calcite, respectively, as a function of temperature; typical curves obtained from the diffusivity data in the present study are compared with experimentally measured thermal conductivities of these materials[7]. Table 4 compares the thermal conductivity values for some of the minerals examined in the present study with results reported in the literature. Several points are to be noted here: (a) the thermal conductivity values obtained from the present study are calculated from experimentally measured thermal diffusivity and density (through use of eqn. 1) in contrast to the literature results which were obtained experimentally; (b) the minerals for which thermophysical data are available in the literature are of different origin and location; (c) the literature data for pyrite and calcite represent both polycrystalline and single crystalline materials.

DISCUSSION

The thermal diffusivities of the minerals examined in the present study in general decrease with increasing temperature. Analcite and potassium feldspar, however, show pronounced maxima in their diffusivity–temperature relationships (Figs. 5 and 6). The trends in their thermophysical behavior are strikingly similar to those reported by Beers et al.[14], on n-type germanium–silicon alloys. These authors invoke the concept of radiative heat transfer to account for the observed behavior; it is possible that similar effects play a role in the case of analcite and potassium feldspar.

The strong anisotropic effects observed in the thermal diffusivity values of plagioclase-2 and -3) and potassium feldspar are attributed to preferred grain orientation effects in these minerals. Scattering of phonon lattice waves at the grain boundaries of the individual crystallites in the mineral matrix in certain preferred directions depending on their orientation, is likely to result in strong anisotropic effects. The thermophysical behavior of polycrystalline mineral aggregates (such as the samples examined in the present study) is thus somewhat different from that of single crystals and layered sedimentary rocks. In the former case, anisotropic effects arise from symmetry considerations of crystallographic planes, whereas in the latter the boundaries in the sedimentary varve structure probably represent regions of high resistance to heat flow[2]. Anisotropic effects are found to be relatively small for the polycrystalline dolomite, calcite and quartz samples examined in the present study, in contrast to the behavior of these materials in single crystalline form[5]. Pyrite and analcite on the other hand show essentially isotropic thermophysical behavior.

The significant differences observed in the diffusivity data for the three types of plagioclase are worthy of note. Variations in chemical composition as shown by a comparison of the elemental analyses for the three samples (Table 1) could account for this anomalous behavior. The problems associated with the heterogeneous nature of naturally occurring materials also seem to be particularly severe with this mineral.

The data shown in Table 4 also reveal significant differences in the behavior of minerals in single crystalline form versus those existing as polycrystalline aggregates. For example, the thermal conductivity of single crystalline pyrite is almost twice that observed for the polycrystalline samples. These differences again reflect the importance of phonon scattering effects at the grain boundaries.

The high thermal diffusivity values characteristic of pyrite relative to the other minerals are also worthy of note. It is likely that Green River oil shales containing significant amounts of pyrite will have rather high thermal diffusivities.

It is instructive to compare the diffusivity data obtained in the present study with those reported in the literature. The diffusivity data reported on quartz employing a radial heat flow method are in good agreement (mean deviation $\pm 8\%$) with the results obtained in the present study by the laser flash technique. The close correspondence of results obtained from two independent measurement techniques is gratifying. Beatty's reported results[16] on powdered dolomite are seen to be appreciably larger than the values observed in the present study (2.32×10^{-3} cm^2 sec^{-1} as compared to the present values of $\sim 1.07 \times 10^{-2}$ cm^2 sec^{-1} at 150°C). This order of magnitude difference arises from the use of powdered materials by Beatty[16]; the presence of voids significantly impedes the heat flow between the individual grains in the powdered material. Tadokoro's[17] calculated value on the thermal diffusivity of dolomitic slag is also somewhat higher than the values experimentally found in the present investigation (the temperature corresponding to the value reported by Tadokoro[17] is not known). Chmura[18] presents data on the thermal diffusivity of plagioclase; he finds values of 1.164×10^{-2} cm^2 sec^{-1} and 1.085×10^{-2} cm^2 sec^{-1} for heat flow corresponding to directions parallel and perpendicular to coring planes, respectively. Again, the temperatures at which these measurements were carried out are not available. The above values are however close to those found at room temperature in the present study (0.75×10^{-2} – 1.17×10^{-2} cm^2 sec^{-1} for plagioclase-1, -2 and -3).

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REFERENCES

1 H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, Oxford, 2nd edn., 1959.
2 Y. Wang, J. DuBow, K. Rajeshwar and R. Nottenburg, *Thermochim. Acta*, 28 (1979) 23.
3 J. A. Hendrickson (Ed.), *Synthetic Fuels Handbook*, Cameron Engineers Inc., Denver, 1975.
4 F. C. Haas and M. T. Atwood, in J. H. Gary (Ed.), *Proc. 8th Oil Shale Symposium*, Golden, Colorado, 1975, p. 95.
5 W. J. Parker, R. J. Jenkins, C. P. Butler and G. L. Abbott, *J. Appl. Phys.*, 32 (1961) 1679.
6 R. L. Rudkin, R. J. Jenkins and W. J. Parker, *Rev. Sci. Instrum.*, 33 (1962) 21.
7 Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Klemens, *Thermal Conductivity*, Vol. 2, Plenum Press New York, 1970.
8 Y. S. Touloukian and E. H. Buyco, *Specific Heat*, Vol. 5, Plenum Press, New York, 1970.
9 K. K. Kelley, S. S. Todd, R. L. Orr, E. G. King and K. R. Bonnickson, *U.S. Bur. Mines, Rep. Invest.*, (1953) 4955.
10 E. G. King, *J. Am. Chem. Soc.*, 79 (1955) 2192.
11 K. Horai, *J. Geophys. Res.*, 76 (1971) 1278.
12 J. W. Stout and R. A. Robie, *J. Phys. Chem.*, 67 (1965) 2248.
13 J. P. Coughlin, *J. Am. Chem. Soc.*, 72 (1950) 5445.
14 D. S. Beers, G. D. Cody and B. Abeles, in *Proc. Int. Cong. on Physics of Semiconductors*, Institute of Physics and the Physical Society, London, 1962, p. 41.
15 S. P. Clark, Jr. (Ed.), *Handbook of Physical Constants*, revised edn., Geophysical Society of America Inc., 1966, Sect. 21, p. 659.
16 K. O. Beatty, Jr., *U.S. A.E.C. Rep. FMPC-471*, July 1, 1954.
17 Y. Tadokoro, *Sci. Dep. Tohoku Imp. Univ.*, 10 (1921) 339.
18 K. Chmura, *Przegl. Ged.*, 19 (1971) 15.