The System Pb-As-S

Composition and Stability of Jordanite

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Silica-tube quenching experiments and gold-tube pressure experiments were used to study phase relations in the PbS-rich portion of the system Pb—As—S. Emphasis was placed on determining the P—T—X stability relations of jordanite, the most Pb-rich of the synthetic Pb—As—S compounds. Jordanite, $Pb_9As_4S_{15}$, is stable below 549 $\pm 3°$ C, at which temperature it melts to galena, liquid, and a sulfur-rich vapor phase. Confining pressures of up to 2 Kb do not measurably change this reaction temperature. Density measurements on synthetic material show that the jordanite cell contains 3 $(Pb_9As_4S_{15})$; space group $P2_1/m$ requires that the cell content be expressed as either $Pb_{28-x}As_{12}S_{46-x}$ or $Pb_{26+x}As_{12}S_{44+x}$, with the former much more probable from a structural point of view. In both cases $0.8 < x < 1.4$ and the situation is thus quite different from the usual case of defect structures, such as pyrrhotite, $Fe_{1-x}S$, which shows considerable range of solid solution. Heating experiments on natural gratonite $(Pb_9As_4S_{15})$ show that this mineral is most probably a low-temperature dimorph of jordanite, the inversion occurring below 250° C. Experiments have also confirmed the extensive substitution of Sb for As in jordanite, as suspected from chemical analyses of the isostructural mineral geocronite $(Pb_{28-x}(As,Sb)_{12}S_{46-x})$.

Durch Abschreckversuche mit Hilfe von Quarz- und Gold-Druckampullen wurden die Phasenbeziehungen im PbS-reichen Teil des Pb—As—S-Systems studiert. Besonderer Wert wurde auf die Feststellung der P—T—X-Stabilitätsverhältnisse des Jordanits, des Pb-reichsten Phase der synthetischen Pb—As—S-Reihe, gelegt. Jordanit $(Pb_9As_4S_{15})$ ist unterhalb 549 $\pm3°$ C stabil, wo er sich semikongruent zu PbS, einer Schmelze und einer schwefelreichen Dampfphase zersetzt. Drucke bis zu 2 kb ergaben keine meßbaren Änderungen dieser Reaktionstemperatur. Dichtemessungen am synthetischen Material weisen darauf hin, daß die Jordanitzelle 3 $\times (Pb_9As_4S_{15})$ enthält. Die Raumgruppe $P2_1/m$ fordert entweder die Formel $Pb_{28-x}As_{12}S_{46-x}$ oder $Pb_{26+x}As_{12}S_{44+x}$, wobei die erstere Form strukturell wahrscheinlicher zu sein scheint. In beiden Fällen ist $0.8 < x < 1.4$ und weicht vom gebräuchlichen Begriff der Defektstrukturen, wie z.B. beim Pyrrhotin $(Fe_{1-x}S)$ ab, wie das bemerkenswerte Mischkristallfeld zeigt. Erhitzen von natürlichem Gratonit $(Pb_9As_4S_{15})$ zeigt, daß dieses Mineral sehr wahrscheinlich eine dimorphe Tieftemperaturphase des Jordanits ist. Die Umwandlung erfolgt unterhalb 250° C. Außerdem wurde eine umfangreichere Substitution von As durch Sb im Jordanit festgestellt, was nach den chemischen Analysen des isostrukturellen Geochronits $Pb_{28-x}(As,Sb)_{12}S_{46-x}$ zu erwarten war.

Introduction

Atomic arrangements in various Pb—As—S and Pb—Sb—S sulfosalt minerals have received considerable attention in recent years. Large portions of the structures of these complex sulfides, especially those near the Pb-ends of the series, consist of distorted "galena-like" arrangements with most of the metal atoms having a coordination number of six (HELLNER 1958; BORN and HELLNER 1960). Many crystal-chemical aspects of these minerals remain to be understood however, and despite the present availability of chemical analyses and structural data, the chemical compositions of only few are known with any degree of certainty. It is unfortunate that few experimental data on the chemical systems involved have been available, although this information appears essential to understanding the complex chemistry of the sulfosalts. The experimental approach was used in this study to determine stable phase assemblages in the PbS-rich portion of the system Pb—As—S. Although this paper is particularily concerned with jordanite, it has been necessary to consider as well certain aspects of the minerals gratonite $(Pb_9As_4S_{15})$ and geocronite.

Previous Data for Jordanite, Geocronite, and Gratonite

The considerable discussion in the literature[1] on the precise cell content of jordanite can be summarized by stating that chemical analyses generally fall within the range $Pb_{26-28}As_{14}S_{46-48}$. The substructure of jordanite proposed by WUENSCH and NOWACKI (1966) contains 10 metal atoms and 10 sulfur atoms, corresponding to $M_{40}S_{40}$ in the true cell. They assumed the cell contains $Pb_{26}As_{14}$ and suggested $Pb_{26}As_{14}S_{46}$ as the cell content. The uncertain cell content of geocronite, shown by DOUGLASS, MURPHY, and PABST (1954) to be isostructural with jordanite and presumably representing a series with varying proportions of antimony and arsenic, might correspondingly be expressed as $Pb_{26-28}(As, Sb)_{14}S_{46-48}$, although a new chemical analysis strongly suggests $Pb_{27}(As,$

[1] See, for example, RICHMOND in: PALACHE, RICHMOND, and WINCHELL (1938); FISHER (1940), and BERRY in: PEACOCK and BERRY (1940).

$Sb)_{12}S_{45}$ (BERRY in: DOUGLASS, MURPHY, and PABST 1954).

Weissenberg films of jordanite studied by BERRY (in: PEACOCK and BERRY 1940) indicated a dimensionally orthorhombic B-lattice in which there were two possible monoclinic primitive cells. Reported monoclinic cell dimensions are given in Table 1. Permitted space

Table 1. *Reported cell dimensions of jordanite*

	1	2	3
a	8.86 Å	8.91 ± 0.03	8.96 ± 0.04
b	31.93	31.71 ± 0.03	31.92 ± 0.01
c	8.48	8.42 ± 0.02	8.45 ± 0.03
β	117° 26′	118° 06′	117° 50′ ± 10′

1. RICHMOND in: PALACHE, RICHMOND, and WINCHELL (1938); setting transformed by BERRY in: PEACOCK and BERRY (1940); transformed from kX to Å.
2. BERRY in: PEACOCK and BERRY (1940); transformed from kX to Å.
3. NOWACKI, IITAKA, BÜRKI, and KUNZ (1961).

groups are $P2_1$ or $P2_1/m$ of which WUENSCH and NOWACKI (1966) concluded $P2_1/m$ the most probable since jordanite does not appear to be piezoelectric and natural crystals show morphology of symmetry $2/m$. Geocronite is monoclinic (probable space group $P2_1/m$) with cell dimensions close to those of jordanite. DOUGLASS, MURPHY, and PABST (1954) confirmed, by single-crystal study, the isostructural relation of these minerals first suspected by SOLLY (1900).

Gratonite, previously considered to have a composition distinct from that of jordanite, is rhombohedral $(R3m)$ with $a_{rh} = 17.69$ Å, $\alpha_{rh} = 114° 05′$ (PALACHE and FISHER 1940). RÖSCH (1963) spectrographically analyzed gratonite from various localities and confirmed the composition $Pb_9As_4S_{15}$ previously determined by chemical analyses. The structure was shown to be related to the PbS lattice when the c axis of gratonite is taken as [111] in PbS. The only experimental syntheses of phases in the system Pb—As—S were undertaken by RÖSCH and HELLNER (1959) by heating mixtures of galena and orpiment with water in quartz tubes. Temperatures varied from 150° to 600° C and pressures from 1 to 1800 atmospheres. Compounds corresponding to several of the known Pb—As—S minerals were synthe-

sized under these experimental conditions. Gratonite was not encountered as a synthetic phase.

Experimental Methods

Two types of experiments were employed for synthesis of phases: 1. silica-tube quenching experiments, which were used to determine relations in the presence of an equilibrium vapor phase, and 2. gold-tube experiments, used to study the effects of confining pressure on phase relations. Both techniques were described in detail by KULLERUD and YODER (1959). Reported heating temperatures for the silica-tube experiments are considered accurate to $\pm 2°$ C and uncertainties in temperatures and pressures of the gold-tube experiments are considered to be $\pm 5°$ C and ± 20 bars respectively. All charges were rapidly chilled to room temperature after the heating period, either by rapidly immersing the sample containers in cold water (silica-tube experiments), or by spraying the cold-seal bombs with a jet of cold water (gold-tube experiments); respective quenching times are estimated as 3—5 seconds and 2—4 minutes.

Spectrographically-analyzed elements (99.999 wt. % purity) were either used directly as reactants, or to prepare PbS and vitreous As_2S_3 reactant material. A great deal of difficulty was encountered in obtaining equilibrium in reasonable lengths of heating time (less than a month) when mechanical mixtures of the elements or PbS and As_2S_3 were used as reactants. To shorten the heating times required, many of the charges were melted to homogeneous liquids in evacuated silica glass tubes and reground to powders prior to annealing at the desired temperatures.

Standard polished-section techniques (the section mounts were prepared from cold-setting resins) and X-ray diffraction powder patterns were used to identify phases. Powder patterns were obtained from smear mounts using $CuK\alpha$ radiation ($\lambda = 1.5418$ Å).

Phase Relations in the Presence of Vapor

Phase relations along the PbS-rich portion of the join PbS—As_2S_3 as determined by quench-
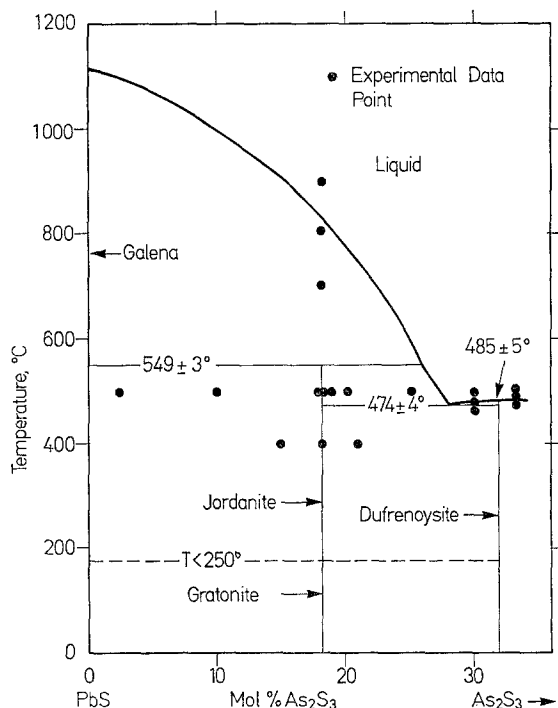

Fig. 1. Phase relations along the PbS-rich portion of the PbS-As_2S_3 join in the presence of vapor

ing experiments are shown in Fig. 1. Three condensed phases were encountered in the room-temperature products: galena, jordanite, and dufrenoysite. These were identified by their characteristic X-ray powder patterns (BERRY and THOMPSON 1962) and by their optical properties in reflected light. The optical properties of the synthetic phases appear identical to those described for the minerals (RAMDOHR 1955). Fine-grained mattes consisting of galena, jordanite, and dufrenoysite encountered in certain of the products were interpreted to have crystallized from liquid during chilling of the charges to room temperature; this textural interpretation is supported by the melted appearance of such charges. Vapor was present as a phase in all silica-tube experiments and was evidenced by a yellow sublimate over the inside walls of the tubes at room temperature. Although no quantitative data on vapor compositions are available, it is highly probable that the composition of the vapor is nearly pure sulfur.

Table 2. *Silica-tube experiments used to determine jordanite composition*

Reactant*	Composition (Mol % As_2S_3)	Temp. °C	Heating Time (hours)	Products
Pb + As + S	18.0	500	69	jordanite + galena + V
PbS + As_2S_3	18.2	500	168	jordanite + V
Pb + As + S	18.6	500	66	jordanite + L** + V
PbS + As_2S_3	18.2	400	480	jordanite + V
PbS + As_2S_3	15.0	400	1080	jordanite + galena + V
PbS + As_2S_3	21.1	400	1080	jordanite + dufrenoysite + V
Pb + As + S	($Pb_{28}As_{12}S_{48}$)	500	48	galena + jordanite + L** + V
Pb + As + S	($Pb_{27}As_{12}S_{43}$)	500	150	galena + jordanite + L_s** + V

* Reactants melted to a homogeneous liquid prior to annealing.

** Liquid crystallized to jordanite and dufrenoysite during quenching. L_s refers to a liquid near pure sulfur in composition.

The composition of synthetic jordanite was determined at 500° C (Table 2). This phase has a very narrow range of composition, expressed as 18.2 ± 0.2 Mol % As_2S_3 on the PbS—As_2S_3 join. Experiments more PbS-rich in composition than 81.8 Mol % PbS contained galena as an equilibrium phase, and those more As_2S_3-rich contained either liquid (above $474 \pm 4°$ C) or dufrenoysite (below $474 \pm 4°$ C). The last two experiments listed in Table 2 show that there is no detectable variation in the (Pb + As): S ratio of synthetic jordanite and that the composition of this phase is therefore confined to the PbS—As_2S_3 composition join.

The extent of solid solution of As_2S_3 in PbS was estimated by measuring the cell edge of PbS equilibrated with jordanite for 18 days at 500° C. The cell edge of the galena was determined by measuring the angular positions of the 531, 600, 620, and 622 X-ray reflections of PbS relative to the 440 and 531 reflections of a CaF_2 internal standard and processing the measurement data by a least squares computer program. The value for the cell edge of the galena was found to be 5.9355 ± 0.0004 Å, in close agreement with the value 5.9358 ± 0.0002 Å found by Bethke and Barton (1961) for the cell edge of synthetic PbS. No solid solution of As_2S_3 in PbS has therefore been shown in Fig. 1.

The composition of the synthetic dufrenoysite encountered in this study was not precisely determined; it lies within the range 30—33 Mol % As_2S_3, somewhat more PbS-rich than the composition $Pb_2As_2S_5$ (33.3 Mol % As_2S_3) assigned to this mineral in Dana's System of Mineralogy (1944).

Heating experiments conducted using synthetic jordanite as reactant show that this phase is stable in the presence of vapor only below $549 \pm 3°$ C; when heated above that temperature, rapid reaction to galena + L + V occurs. Since the vapor volume in all experiments was reduced to a minimum by snuggly-fitting glass rods (as described by Kullerud and Yoder 1959), the compositions of the condensed phases (jordanite, galena, and liquid) lie essentially on the PbS—As_2S_3 join and the decomposition point of jordanite therefore involves three compositionally-colinear phases. Melting

points of this type have been termed semi-congruent by RICCI (1951, pp. 305—306). No difficulty was encountered in precisely determining the temperature of this reaction point by quenching experiments, since virtually no reequilibration of the galena and liquid occurred during the rapid chilling of the charges to room temperature.

Phase relations at temperatures above and below the melting point of jordanite can be further understood by reference to Fig. 2. These
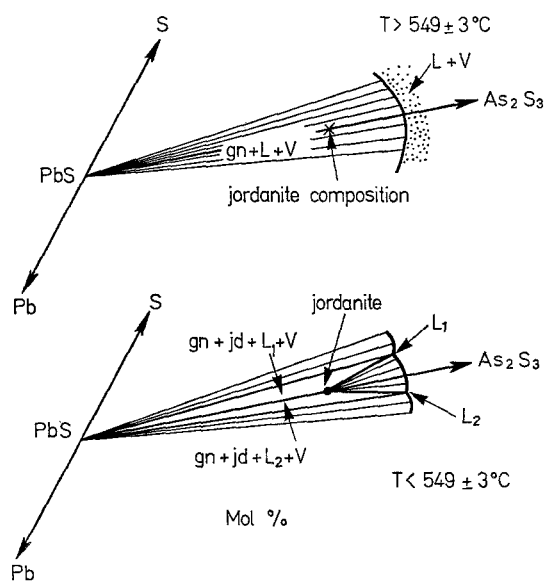

Fig. 2. Phase relations in a portion of the ternary system at temperatures slightly above and below the melting point of jordanite

relations are inferred from those determined along the PbS—As$_2$S$_3$ join and through consideration of permissible geometries of solid-liquid phase relations. Two distinct galena $+ L + V$ assemblages (differentiated by liquid compositions L_1 and L_2) are stable below 549°C; the compositions of L_1 and L_2 approach the PbS—As$_2$S$_3$ join with increasing temperature and coalesce on that join at 549° C. Above that temperature a single galena $+ L + V$ field spans the composition of jordanite on the PbS—As$_2$S$_3$ join.

The Singular Behaviour of Jordanite in P-T-X Space

Four phases (jordanite, galena, liquid, and vapor) containing three components are in equilibrium at the melting point of jordanite, and application of the Phase Rule $(F = C - P + 2)$ might lead us to conclude that the system possesses one degree of freedom. An additional restriction must be imposed, however, since three of the four phases present are compositionally colinear and, as discussed by RICCI (1951, pp. 24—29), the variance (F) becomes zero by restriction. Systems of this type, which contain compositionally colinear phases, are defined as singular systems and the melting point of jordanite referred to as a singular point rather than as an invariant point. Although $F = 0$ by restriction at a singular point, the thermodynamic nature of such points is not equivalent to the usual situation where $F = 0$ because $C + 2$ phases coexist in equilibrium. It is important to appreciate the difference.

Consider an isolated invariant system. Any change in temperature $(d\text{T})$ or pressure $(d\text{P})$ will cause a reaction to occur among certain of the phases present such that P and T tend to return to their original values as defined by the position of the invariant point in P—T—X space. Pressure and temperature are thus buffered by the invariant phase assemblage, or stated another way, the equilibrium state of the system (characterized by the number and compositions of the phases present) is independent of the relative amounts of the phases. Singular systems, on the other hand, are incapable of any such buffering action — the small changes $d\text{T}$ and $d\text{P}$ will cause either a change in composition of one of the phases present or loss of one of these phases, i.e., a change in the equilibrium state of the system will occur. For the case in point, a small decrease in pressure (perhaps more easily understood as an increase in volume) over the assemblage galena $+$ jordanite $+ L + V$ will cause sulfur and arsenic to volatilize from the liquid phase, which must correspondingly change in composition.

The difference between singular and invariant points is reflected in the geometrical arrangement of univariant curves around such points
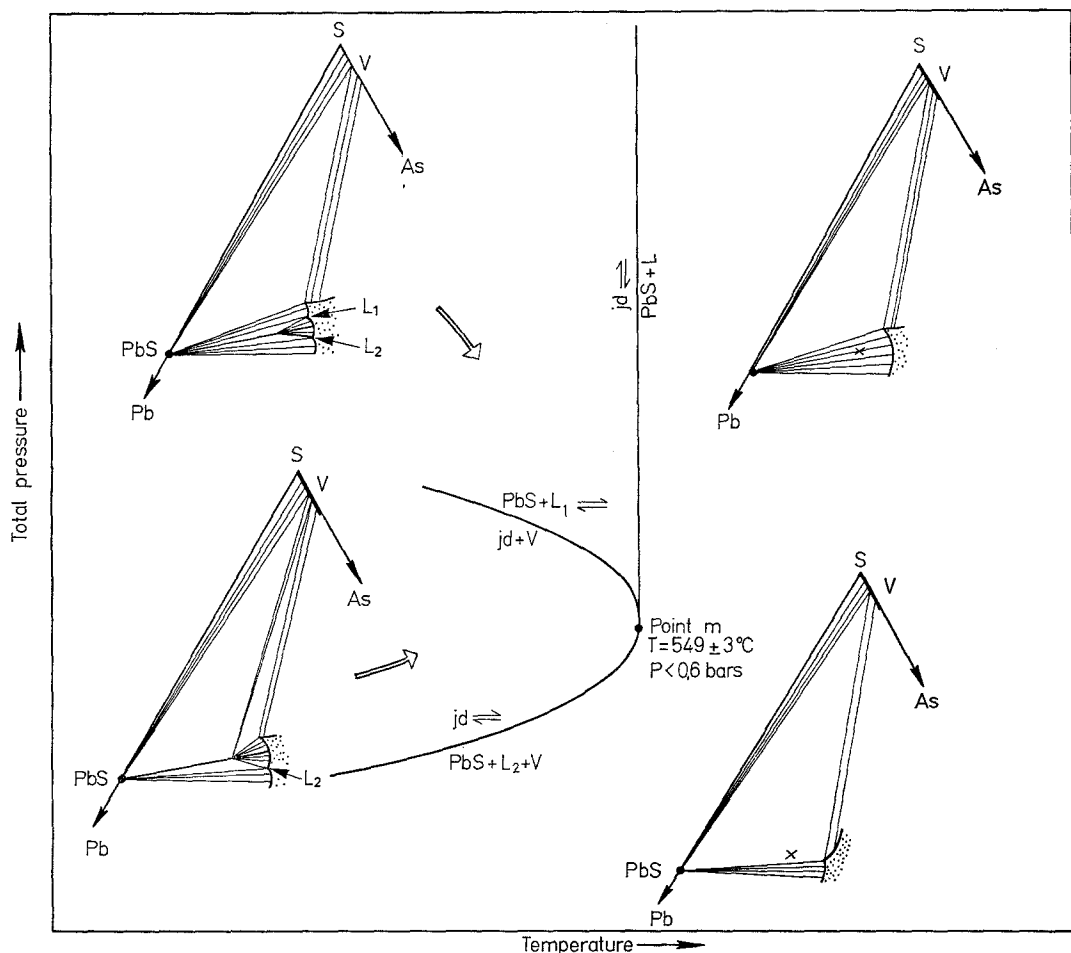
Fig. 3. The P-T projection of the singular melting point of jordanite. The compatible phases within each P-T field are connected by tielines on the accompanying schematic ternary diagrams

on P—T projections of P—T—X space. The arrangement of curves around the singular melting point of jordanite (Fig. 3) was deduced through consideration of the phase relations shown in Figs. 1 and 2. Below 549° C, there are two distinct univariant assemblages which include jordanite as a stable phase — galena + jordanite + L_1 + V and galena + jordanite + L_2 + V. Since the compositions of L_1 and L_2 coalesce with increasing temperature, the univariant curves for these assemblages must imperceptably merge at Point m (the singular melting point of jordanite) with no abrupt change in slope when viewed on the P—T projection. The univariant curve for the assem-

blage containing L_1 must lie at higher pressures than that for the assemblage containing L_2 since L_1 contains a higher percentage of sulfur than L_2. It is anticipated that the curve for the galena + jordanite + L_1 + V assemblage will terminate below 549° C at an invariant point with composition on the sulfur-side of the join PbS—As_2S_3, which will involve a sulfur-rich liquid of relatively high vapor pressure. This curve has therefore been shown extending from Point m to higher pressures at lower temperatures. A vapor-absent curve, defining the temperature of the reaction jordanite $\rightleftharpoons$ galena + L as a function of pressure, must also originate at Point m; this curve is uni-

variant by restriction since the three
phases present are compositionally colinear.
Because vapor is absent as a phase, and the
volume change in the reaction jordanite
$\rightleftharpoons$ galena $+ L$ probably slight, this curve will
be steep as viewed on the P—T projection.
The experimentally determined curve is dis-
cussed below. It is of interest to note that
no univariant curves (other than the vapor-
absent curve) originate at the singular point
and extend to higher temperatures and
pressures. This feature of the P—T projec-
tion of the jordanite melting point is a general
feature of all singular melting points. Around
an invariant point, however, one or more
curves including vapor as a phase must ex-
tend from the invariant point to higher tem-
peratures and pressures.

Although the temperature of Point m is
known with a precision of $\pm 3°$ C, no ex-
perimental data are available to reliably esti-
mate the vapor pressure at that point. A
maximum value can, however, be taken as
the pressure over a liquid of pure sulfur com-
position at the same temperature. A calculat-
ed value about 0.6 bars is obtained by
using the equation for sulfur vapor pres-
sure versus temperature given by WEST (1950).

Effect of Confining Pressure on the Melting Point of Jordanite

Gold-tube experiments under confining pres-
sures of 1 and 2 kilobars were used to investi-
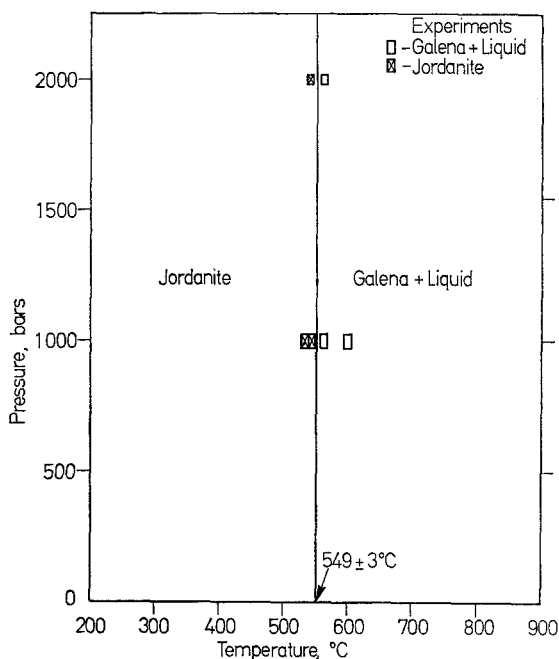gate the effect of pressure on the melting reac-

Fig. 4. The experimentally determined P-T curve for
the reaction jordanite $\rightleftharpoons$ galena $+$ liquid

tion jordanite $\rightleftharpoons$ galena $+ L$. The experiments
used to determine the melting curve (the vapor-
absent curve, (V), in Fig. 3) are reported in
Table 3 and the melting curve is shown in
Fig. 4. No evidence was noted of reaction be-
tween the gold sample containers and either
galena or jordanite. The fine-grained inter-
growths of galena, jordanite, and dufrenoysite

Table 3. *Gold-tube experiments under confining pressure. Synthetic jordanite,*
$Pb_9As_4S_{15}$, *used as reactant in all experiments*

T° C	P, bars	Heating Time (hours)	Results
600	1000	93	galena + liquid*
556	1000	18	galena + liquid*
547	1000	504	reactant unchanged
538	1000	18	reactant unchanged
560	2000	49	galena + liquid*
550	2000	219	reactant unchanged

* The liquid crystallized to PbS, dufrenoysite, and gold during
quenching of the charges to room temperature. An estimated 2 vol.%
Au is present in the resulting dendritic intergrowths.

(crystallized liquid) always contained, however, an estimated 2 volume percent gold intergrown with the other phases in a dendritic pattern. The effect of this gold content of the liquid phase has been assumed negligeable, since the extrapolation of the determined curve to low pressures yields a predicted temperature for Point m of 550 $\pm$ 10° C (the measured value is 549 $\pm$ 3° C). The experimentally-determined melting curve is vertical within the uncertainty of measurement, and confining pressure therefore has essentially no effect on the jordanite melting reaction.

Discussion of the Cell Content of Jordanite

The observed composition of synthetic jordanite on the PbS—As$_2$S$_3$ join (18.2 $\pm$ 0.2 Mol % As$_2$S$_3$) corresponds to the composition 9 PbS · 2As$_2$S$_3$ or Pb$_9$As$_4$S$_{15}$. Density measurements of the synthetic phase were used to determine the cell content. The mean of eight density measurements using a Berman balance was 6.15 grams/cm^3 with a standard deviation of the mean of $\pm$ 0.03 grams/cm^3. The calculated density for jordanite using the cell dimensions reported by NOWACKI et al. (1961) (Table 1) and assuming the cell contains3 (Pb$_9$As$_4$S$_{15}$) is 6.16 grams/cm^3, in excellent agreement with the measured value. The agreement between the measured value and that calculated using the cell dimensions reported by BERRY (6.30 grams/ cm^3) is much less satisfactory; the discrepancy can be explained, however, if it be assumed that the material studied by BERRY contained antimony (see below). It seems reasonably certain, on the basis of the composition and density of synthetic material, that the jordanite cell contains Pb$_{27}$As$_{12}$S$_{45}$. Further supporting evidence is provided by the analysis of geocronite from Park City, Utah, provided by DOUGLASS, MURPHY, and PABST (1954). That analysis yields a calculated cell content for geocronite of Pb$_{27.09}$(As, Sb)$_{11.89}$S$_{45.25}$, very close to that determined in this study for the isostructural jordanite end-member of the series.

The density of synthetic jordanite (6.15 grams/ cm^3) is considerably lower than values reported in the literature for the density of natural material (6.38 $\pm$ 0.05 grams/cm^3). Two possible

explanations exist for the discrepancy. The density determinations by BERMAN (in: FISHER 1940) and BERRY (in: PEACOCK and BERRY 1940), 6.38 $\pm$ 0.01 and 6.44 grams/cm^3 respectively, were made on unanalyzed material that possibly contained several percent antimony. The measured densities of synthetic jordanite and geocronite (see below) and of one analyzed natural geocronite are plotted as a function of Sb-content in Fig. 5. This diagram is presented
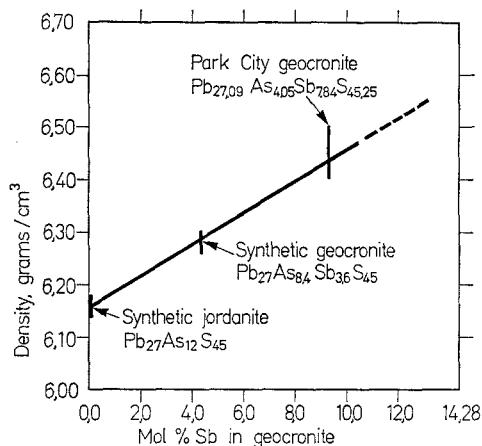

Fig. 5. The variation of density with composition along the geocronite solid solution series. The densities of the synthetic material are from this study, and the density of geocronite from Park City, Utah, is from DOUGLASS, MURPHY, and PABST (1954). The length of the vertical bars represents the uncertainty of the measurements

to demonstrate that the substitution of Sb for As along the geocronite solid-solution series is accompanied by a measurable increase in density. The discrepancy with the densities of analyzed material determined by JACKSON (6.413 grams/cm^3, in: SOLLY 1900) and by KAWAI (6.451 grams/cm^3, reported in: The System of Mineralogy, 1944) is more difficult to explain. Possibly their material was not homogeneous, since SCHNEIDERHÖHN and RAMDOHR (1931, p. 444) reported that most natural specimens of jordanite contain inclusions of two additional phases, one of which is probably galena. Only a few percent included galena would be necessary to raise the observed density from 6.15 to 6.40 grams/cm^3.

The possible space groups for jordanite, $P2_1$ or $P2_1/m$, both contain only even-fold positions, so that a cell content $Pb_{27}As_{12}S_{45}$, which represents odd numbers of atoms, cannot refer to an ordered structure[2]. Symmetry reasons thus necessitate writing the cell content as $Pb_{28-x}As_{12}S_{46-x}$, or much less likely from a structural point of view, as $Pb_{26+x}As_{12}S_{44+x}$. In both cases $0.8 \geqq x \geqq 1.4$. A complete structural determination is needed before we can choose between the two ways of writing the cell content; the partial structure determined by WUENSCH and NOWACKI (1966) indicates, however, that $Pb_{28-x}As_{12}S_{46-x}$ is the more probable since, based on the subcell, they proposed that the true cell contains a total of 40 (Pb + As) atoms.

The interesting aspect of the cell content of jordanite is that although vacant positions must be present in the structure, the composition range of this phase seems exceedingly narrow. Moreover, the observed composition centers about a value that happens to give integral subscripts to the three constituent elements. Thus if it were not for space group information, there would be no reason to suspect that $Pb_{27}As_{12}S_{45}$ is not the correct way of writing the cell content. The situation is quite different from the usual case of defect solid solutions such as pyrrhotite, $Fe_{1-x}S$, which show considerable range of solid solution. There is, however, at least one analogous case in the chemical literature, namely Pr_6O_{11} (McCULLOUGH 1950), which has the fluorite structure. Thus for symmetry reasons alone, the cell content should be expressed not as Pr_6O_{11}, but as Pr_6O_{12-x} with $x = 1.00$. No deviation from stoichiometry is observed in this compound.

[2] By similar reasoning, DOUGLASS, MURPHY, and PABST (1954) pointed out that the structure of geocronite probably also involves vacancies in atomic sites.

The Relation of Jordanite and Gratonite

A question raised by the experimental results concerns the relation of the minerals jordanite and gratonite. That the experimentally-determined composition of jordanite can be expressed as $9 PbS \cdot 2As_2S_3$ (the same as that accepted for gratonite) suggests that gratonite is a low-temperature modification of jordanite, although it might as well be suspected that some element in addition to Pb, As, and S is necessary to stabilize gratonite relative to jordanite. The spectrographic analysis of gratonite by LUNDAHL (in: PALACHE, and FISHER 1940) showed the absence of Bi, Ir, Co, and Ni, less than 0.01 % Fe, less than 0.1% each of Mg, Mn, and Sn, and about 0.1% Sb. It seems unlikely that the composition of gratonite must be altered to include these trace amounts of additional elements. No experiments were undertaken in this study to synthesize gratonite below 400° C since the rate of reaction in the dry system would necessitate months or perhaps years of heating time to approach equilibrium. Several
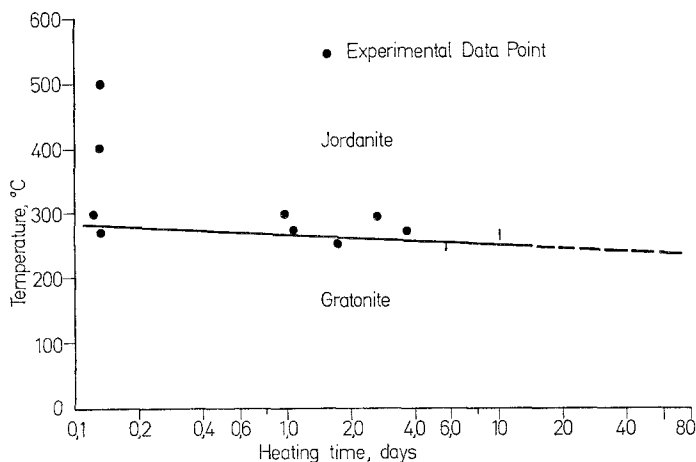

Fig. 6. Temperature versus time reaction rate curve for the reaction gratonite → jordanite

heating experiments using natural gratonite as reactant material were, however, undertaken in an effort to determine something of the stability of this mineral. The results of these experiments are shown graphically in Fig. 6. Gratonite was

converted to jordanite in heating periods that increase logarithmically with decreasing temperature; only about three hours were required for complete conversion to jordanite at 300° C, whereas several days heating were necessary at 250° C. The curve shows that the heating time necessary for the reaction gratonite → jordanite to go essentially to completion (judged by the presence or absence of gratonite X-ray reflections in powder patterns) increases by a factor of 4 to 5 for every 10° C decrease in temperature. Careful examination of the polished sections of jordanite synthesized by heating gratonite did not reveal the presence of small amounts of galena or dufrenoysite which could be taken as evidence for a compositional difference between the two phases. Based on the chemical and spectrographic analyses of gratonite in the literature, and on the experimental results of this study, it is concluded that gratonite and jordanite are dimorphs and that the inversion temperature is below 250° C.[3]

Synthetic Geocronite

A few experiments (Table 4) having compositions within the quaternary system Pb—As—Sb—S were undertaken to confirm the extensive substitution of antimony for arsenic in synthetic jordanite as suspected from the chemical

[3] Note added in proof: It has been brought to my attention that investigations of natural gratonite by BURKART, I,. J. OTTEMANN, and B. NUBER: N. Jb. Min., Mh., (in press) have shown that gratonite and jordanite may have the same chemical composition.
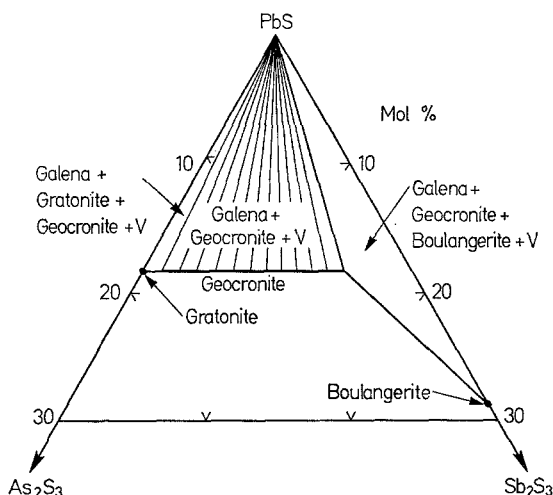

Fig. 7. Phase relations in the $PbS-As_2S_3-Sb_2S_3$ plane of the quaternary system Pb—As—Sb—S at 500°C. The orientation of tielines and the exact position of Point a were not determined

analyses of the isostructural mineral geocronite. Homogeneous geocronites having compositions $Pb_{27}As_{8.4}Sb_{3.6}S_{45}$ and $Pb_{27}As_6Sb_6S_{45}$ were readily prepared along the composition join $Pb_{27}As_{12}S_{45}-Pb_{27}Sb_{12}S_{45}$. An attempt to synthesize a $Pb_{27}Sb_{12}S_{45}$ end-member of the series, corresponding to the mineral variety schultzite[4], was not successful; the equilibrium

[4] Schultzite is reported in: The System of Mineralogy (1944, p. 396) as an arsenic-free variety of geocronite, ". . . the validity of which is not yet established".

Table 4. $PbS-As_2S_3-Sb_2S_3$ experiments

Composition	Reactant*	T, °C	Heating Time (hours)	Products
$Pb_{27}Sb_{12}S_{45}$	1	664	48	galena + L** + V
$Pb_{27}Sb_{12}S_{45}$	1	500	432	galena + boulangerite + V
$Pb_{27}As_{8.4}Sb_{3.6}S_{45}$	2	500	45	geocronite + V
$Pb_{27}As_6Sb_6S_{45}$	2	500	264	geocronite + V

* Key to reactant materials: 1. Fine-grained intergrowth of galena and boulangerite synthesized by rapidly chilling homogeneous liquid. 2. A mixture of synthetic jordanite and Reactant 1.

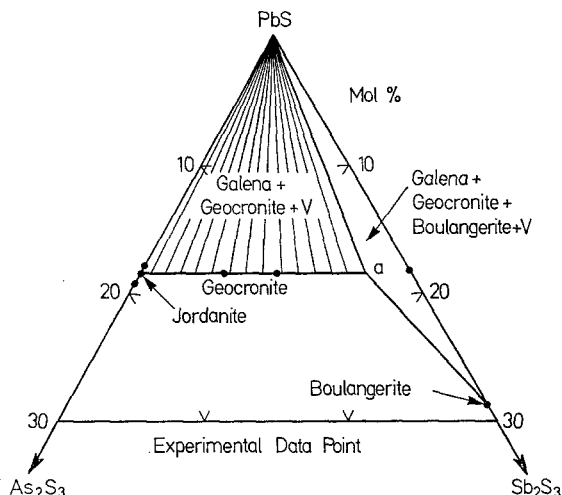** Liquid crystallized to galena and boulangerite during quenching.

Fig. 8. Schematic phase relations in the PbS—As$_2$S$_3$—Sb$_2$S$_3$ plane below 250° C

assemblage having bulk composition Pb$_{27}$Sb$_{12}$S$_{45}$ was galena $+L+V$ at 664° C and galena $+$ boulangerite $+V$ at 500° C. Phase relations in the PbS—As$_2$S$_3$—Sb$_2$S$_3$ plane as interpretated from the above experiments are shown in Fig. 7. It has been assumed in drawing this diagram that the PbS:(As$_2$S$_3$, Sb$_2$S$_3$) ratio in geocronite is constant at 9:2 as is the case for the jordanite end-member of the series.

It might be worthwhile to consider a possible phase diagram for the PbS—As$_2$S$_3$—Sb$_2$S$_3$ plane at some low temperature where gratonite is a stable phase on the PbS—As$_2$S$_3$ join. A tentative diagram, representing little more than la guess, is shown in Fig. 8. This diagram is drawn to explain the observed mineral assemblages galena $+$ gratonite and galena $+$ "jordanite" if it is assumed that the jordanite in the latter assemblage actually contains antimony. Support for the proposed galena $+$ boulangerite $+$ geocronite $+$ V assemblage is provided by RAMDOHR (1955), who noted that low-temperature alteration of geocronite may produce a mixture of galena and boulangerite. Such alteration could result either from reequilibration of an Sb-rich geocronite solid solution to a more As-rich member stable at low temperatures, or by removal in solution of As$_2$S$_3$ from geocronite.

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