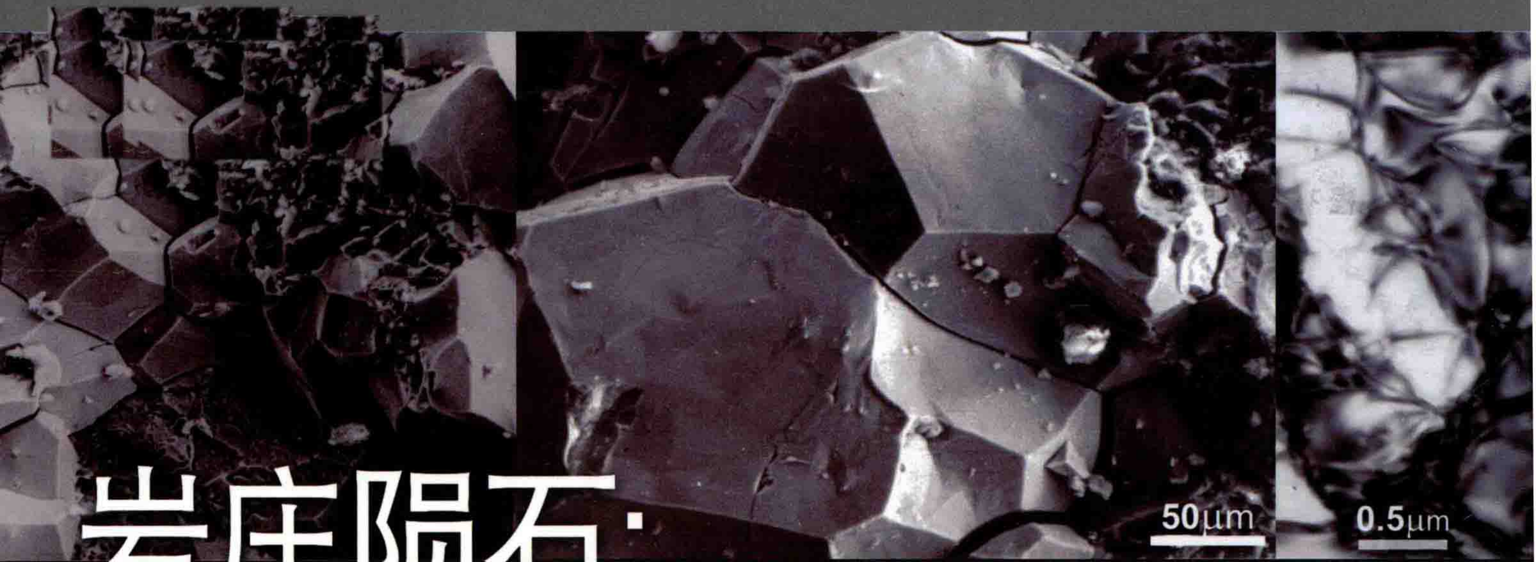

岩庄陨石：矿物学与冲击变质

Yanzhuang Meteorite: Mineralogy and Shock Metamorphism

谢先德　陈鸣　著

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我很同意你们的看法，岩庄陨石确实是世界上受冲击最严重的一块特殊陨石。

国际地球化学和宇宙化学协会主席、德国马普化学研究所所长
Heinrich Wänke，1992. 8. 26

岩庄陨石是一块奇异的陨石，这是我第一次见到具冲击熔融物质最多的一块普通球粒陨石。

国际陨石学会主席、美国加州大学洛杉矶分校教授
John T. Wasson，1992. 9. 1

前言

Preface

小行星、流星体或陨石母体之间的高速碰撞可导致冲击波作用范围的岩石矿物发生冲击变质。研究冲击变质作用下陨石和矿物的冲击效应，对探索星体演化、高温高压地质学、材料科学等具有重要意义。过去的研究表明，在宇宙空间经受过高能冲击碰撞的球粒陨石大多属于L群的，LL群球粒陨石比L群的要低得多，被强烈冲击过的H群球粒陨石是比较罕见的。陨落在广东翁源县的岩庄陨石是不久前在我国收集到的经过极端高能冲击、具有大量冲击熔融物质和强烈变形未熔融物质的H群球粒陨石。

为了探讨在冲击波作用下岩庄陨石的冲击效应，我们利用一系列微矿物学的技术和方法，包括光学显微镜、相差显微镜、扫描电子显微镜、透射电子显微镜、电子探针、激光拉曼探针、X射线衍射分析、原位微区X射线衍射分析、中子活化分析、激光剥蚀等离子质谱分析和质子诱导X射线发射分析等，对岩庄陨石的矿物学和冲击变质特征进行了深入的研究，重点放在各矿物相的微结构、表面微形貌和化学成分特征，以及冲击熔体的矿物组合和常量与微量元素化学组成上，从而揭示出该陨石的冲击压力温度历史和熔融后元素的再分配上。

研究查明，岩庄陨石在距今2.6 Ma的一次小行星碰撞事件中离开了它的母体，碰撞时的速度达到7～8 km/s，碰撞在岩庄陨石中产生的冲击波峰压最高达到>60 GPa，冲击温度达到2 000℃。

基于岩石学、矿物结构和矿物化学特征的研究，我们确定岩庄陨石属于典型的H群球粒陨石，岩石类型为H6， 局部为H7。综合其岩石和矿物的冲击变质特点，我们将岩庄陨石划分出4个变质程度不同的冲击相：冲击熔融及重结晶相（M）、极强冲击相（S6）、强冲击相（S5）、中等强度冲击相（S4）。这说明小行星撞击使岩庄陨石经受了非常不均匀的压力和温度作用，由于复杂的压力和温度脉冲及传播，使得陨石中不同区域的岩石和矿物产生了非平衡的冲击效应：①在冲击波作用相对较弱的区域，橄榄石和辉石中发育4～5组面状裂隙；随着压力的增加，这两种矿物中的螺型位错密度从10^{-3} mm^{-2}增大到10^{-7} mm^{-2}，镶嵌状结构的粒度从20 μm变小到2 μm；斜长石部分转变为击变玻璃；铁纹石和镍纹石中发育有多组纽曼线；陨硫铁中出现镶嵌状结构。②在冲击作用较强区域，以强拉伸为主部位中的橄榄石和辉石发生矿物粒内砾化和无序化；以高温作用为主部位中的橄榄石和辉石发生广

泛的固态重结晶和位错攀移；在高温高压明显部位，橄榄石和辉石转变为击变玻璃、熔融玻璃，或相变为其高压多形；一些高温区中的铁纹石和镍纹石发生淬火形成马氏体，或发生熔融和重结晶；陨硫铁普遍发生熔融重结晶。③在冲击的最强烈作用区域，陨石发生原地的整体熔融和部分重结晶，形成黑色的冲击熔脉和熔块；熔脉和熔块的组成矿物主要为重结晶的橄榄石和辉石微晶、FeNi金属+ FeS的共结体团块、硅酸盐熔体玻璃，以及少量原球粒陨石的残留矿物晶屑等；局部还可以观察到硅酸盐、FeNi金属和硫化物等多种陨石矿物，发生了一定程度的分解和气化；大部分固化重结晶的FeNi金属淬火形成奥氏体和马氏体。

除上述主要成果外，我们对岩庄陨石的微矿物学研究还有如下重要新发现：

（1）首次于1992年在陨石中找到了天然的橄榄石和辉石的击变玻璃。橄榄石击变玻璃存在有1 108 ~ 1 116 cm^{-1}和1 180 ~ 1 188 cm^{-1}两个较强的拉曼谱带，而辉石击变玻璃存在有818 ~ 840 cm^{-1}附近一个宽阔的弱拉曼谱带。

（2）早在1992年，第一次在H群球粒陨石中发现了橄榄石的高压相林伍德石和辉石的高压相镁铁榴石。查明林伍德石具有两种产状。一种是从橄榄石击变玻璃中原地成核结晶的它形和亚圆形林伍德石微晶，另一种是从硅酸盐熔体中结晶析出的自形粒状林伍德石。研究还发现，在冲击波卸载后，超过90%的林伍德石逆转变为常压相（α相）。镁铁榴石的形成也经历了从击变玻璃中原地成核和结晶的过程，并且大部分在后期发生了崩解和重结晶转变返回辉石结构。

（3）首次在陨石中发现强烈的冲击波作用，导致了陨石中的辉石及其高压相发生结构变异和结构重组，其结果是在晶粒内部形成以重结晶结构为主，兼具有孤立硅氧四面体、三桥氧和全桥氧硅氧四面体基团混合组合的变异结构。

（4）首次在陨石中发现包括橄榄石、低钙辉石、FeNi金属和陨硫铁在内的一整套由气相或气液相冷凝结晶而形成的矿物自形晶体，并根据表面微形貌特征，首次提出了一种气相结晶FeNi晶须和液相结晶FeNi针的特殊螺旋状生长模式。

（5）首次在岩庄陨石冲击熔体的固化重结晶FeNi金属颗粒中，发现了一种呈非对称性及方向性分布的三带微结构和Ni含量呈台阶状分布的模式，而在熔块中的金属—陨硫铁共结体团粒内，绝大部分FeNi金属粒具有壳—核对称分布的两个微结构带，即马氏体的内带和富Ni边，穿过二个微结构带的Ni含量呈“M”形分布，查明二者微结构的差别，主要与它们的冷却速率不同有关。

（6）首次在FeNi金属枝晶的头部表面发现有特征的四同心环生长结构，及由此形成具有多层分枝的阵列式金属枝晶，提出了四同心环结构是太空微重力环境下，远离热力学平衡态的FeNi金属熔体凝固结晶时的一种基本时空图像的新观点。

（7）发现岩庄陨石冲击熔体中产有一种独特的FeNi金属 + FeS + Fe–Mn–Na磷酸盐 + 无铝铬铁矿的共结体矿物组合，首次查明该组合中的磷酸盐矿物有三种，即磷铁锰矿、伽利略矿和一种成分为$Na_2(Fe,Mn)_{17}(PO_4)_{12}$的未知新磷酸盐矿物，而从熔体重结晶的铬铁矿则完全不含有铝。

（8）中子活化分析首次揭示了采自岩庄陨石不同冲击变质程度部位的样品，包括冲击熔脉、熔块和未熔陨石等，在常量和微量元素组成上均十分相似，除少量元素在熔体相和未熔相之间有轻度再

分布外，没有发现金属—硅酸盐或硫化物—硅酸盐之间存在很明显的元素分馏作用证据，说明熔体相是由未熔相原地熔融和快速冷却形成的，同时也说明冲击作用涉及的时间、程度和范围是有限的。

（9）激光剥蚀等离子体质谱分析结果揭示，岩庄陨石受冲击局部熔融后，Fe、Co和Ni等亲铁元素主要富集在熔体内的FeNi金属相中，而Cr、V、Ti和Mn等则进入硅酸盐熔体中；Cu、Ga和Pb等亲铜元素大部分都富集在FeNi金属相内， Zn虽有少量丢失，但主要进入硅酸盐熔体相；Sc、Zr、Nb和Ta等亲石元素，基本上都赋存在硅酸盐熔体相中，Nb比Ta更为活泼；熔体的稀土元素分布具奇偶效应，呈现轻稀土富集、重稀土亏损的特点，而FeNi金属中则轻稀土相对亏损，稀土元素特别是轻稀土元素主要赋存在硅酸盐熔体中；铂族元素在陨石熔融后转移到FeNi金属相中。

（10） FeNi+FeS共结体团粒刻蚀表面的PIXE分析证实，岩庄陨石的FeNi金属枝晶体存在有核-壳微结构，其内核由铁纹石（α-FeNi）和马氏体组成，而外壳则由镍纹石（γ-FeNi）和合纹石组成。FeNi金属枝晶体不含S，其微量元素含量都很低，除Cr达到200 μg/g外，P、K、Ca、Cu、Zn、As、Ge和Se的含量均小100 μg/g。FeNi金属枝晶体间的间隙为陨硫铁充填，其所含微量元素最为丰富， 如Cr的含量可达600 ~ 1 300 μg/g，Cu、Zn和Se等含量也较高。

（11）发现冲击波强烈地改变着岩庄陨石的热释光性质，其自然热释光强度随着冲击压力的加大而减少，热释光的灵敏度也在降低， 峰温和半高宽温度则偏高。在用β射线辐照岩庄陨石样品诱发的热释光，其峰位随辐照剂量的加大而有规律地向低温方向移动。

（12）发现受12 ~ 133 GPa的人工冲击的H群吉林陨石回收样品中产生的变形和变质特征，与岩庄陨石的相关的4个不同冲击相的冲击效应很类似，从而提出了可利用与人工冲击实验样品中发现的类似特征对比，来推定天然受冲击陨石各冲击相P-T历史的新观点，并由此推定出岩庄陨石在太空中经受过的最高冲击压力达到>60 GPa，最高冲击温度达到2 000℃。

本书主要研究成果是在国家自然科学基金委员会41172046项目、40772030项目、40272028项目和广东省科学基金91847项目的资助下完成的。本书作者衷心感谢中国科学院广州地球化学研究所对本项研究的全力支持，感谢李肇辉、刘京发、胡瑞英等研究员在岩庄陨石陨落现场的及时调查和样品收集，以及对岩庄陨石的相关研究。感谢张红博士在岩庄陨石LA-ICP-MS分析上的大力协助， 并与本书第一作者共同完成了本书第十二章的编写，作者同时要感谢中南大学的谷湘平教授在矿物微区X射线衍射分析和部分金属矿物鉴定上的鼎力协助，感谢本所陈林丽工程师陨石矿物的电子探针成分分析上的大力帮助。

谢先德

2017年10月

EXTENDED ABSTRACT IN ENGLISH

Hypervelocity collisions between asteroids, presumably chondritic parent bodies, can cause the shock metamorphism of rocks and minerals in sphere of action of shock wave. The studies on the shock effects of rocks and minerals in structures, chemical composition, solidification and crystallization characteristics have great significance in the investigation of evolution of celestial bodies, geology of high pressures and high temperatures, as well as in material sciences. It is well known that the L group chondrites are more heavily shocked than H and LL group chondrites, and only detailed systematic petrographic and mineralogical studies on shock effects in L group chondrites, especially the L6 chondrites, were carried out during the last twenty of years, but studies on shock effects in H group chondrites are rarely done for the rarity of strongly shocked H group meteorites.

The Yanzhuang meteorite is a very strongly shocked stony meteorite, which fell on October 31, 1990 in Yanzhuang, Wengyuan County, Guangdong Province, China. Right after the fall of this meteorite, a group of scientists from the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), namely, Zhaohui Li, Jingfa Liu and Ruiying Hu, conducted field survey and collection of Yanzhuang meteorite samples. Five pieces in total weight of 3.5 kg of this meteorite was collected. The largest piece is of 823 g in weight. This meteorite is composed of light-colored severely deformed chondritic host and dark-colored thick melt veins (up to 1.5 cm in width) and large melt pockets (up to 3 cm × 4 cm × 2 cm in volume). This implies that Yanzhuang meteorite had been subjected to a violent impact event in space.

A group of scientists headed by Professor Xiande Xie in the Guangzhou Institute of Geochemistry, CAS, then conducted a series of study on collected samples, especially, Dr. Ming Chen completed his Ph.D thesis on "Micro-mineralogy and Shock Effects of the Yanzhuang Meteorite" in 1992. It was confirmed that the Yanzhuang meteorite is a unique chondrite with most abundant shock-induced melt (more than 30% in volume) among all known shock-melt-bearing chondritic meteorites.

The modern micro-mineralogical experimental techniques, including SEM, TEM, EPMA, Raman microprobe spectroscopy, instrumental neutron activation analysis, X-ray micro-diffraction analysis, micro-PIXE analysis and laser ablation ICP-MS, have been used to investigate the mineralogy and the shock effects of the Yanzhuang chondrite. The micro-structural and micro-morphological characteristics as well as chemical composition of minerals (phases) were studied in detail.

This meteorite was classified as an H6 chondrite on the basis of chemical composition and petrologic features, and evaluated as a very strongly (S6) shock-metamorphosed meteorite. The mineral constituents of this meteorite include olivine (40%), low-Ca pyroxene (30%), clinopyroxene (4%), plagioclase (4%), kamacite (10%), taenite (4%), troilite (6%), and small amount of merrillite and chromite.

A shock-induced inhomogeneous temperature-pressure distribution in the Yanzhuang meteorite had led to different shock effects:

(1) In the weaker action areas of shock wave (25 ~ 35 GPa): olivine and pyroxene display 4 ~ 5 sets of planar fractures, high screw dislocation density (from 10^3 mm^{-2} to 10^7 mm^{-2}), small size of mosaic blocks (from 2 μm to 20 μm) and greater difference in crystallographic orientation between neighboring mosaic blocks (from 1° to 10°); plagioclase had partially been transformed into maskelynite; several sets of Neuman lamellae are observed in kamacite and taenite; mosaicism in troilite is widely spread.

(2) In the stronger action areas of shock wave (45 ~ 60 GPa): the brecciated and disorder structures in olivine and pyroxene grains were produced in the prevailing areas of stretching stress; the solid-state recrystallization and dislocation climbing of olivine and pyroxene were induced in the areas of higher temperature; olivine and pyroxene were transformed into diaplectic glass, melt glass and high-pressure phases in the areas of higher pressures, higher temperatures and fast cooling; kamacite and taenite were partially quenched into martensite, or partially melted and recrystallized; an extensive melt and recrystallization of troilite were produced.

(3) In the strongest action areas of shock wave (>60 GPa): the bulk material of chondritic host was melted, forming dark thick melt veins and large melt pockets which were composed of microlites of recrystallized olivine and pyroxene, FeNi + FeS eutectic blobs in different forms and sizes, silicate melt glass and some remained mineral detritus of chondrite; dissociation and vaporization of many kind of minerals including silicates, FeNi metal and sulfides, took place to a certain extent; the solidified and recrystallized FeNi metal were mostly quenched into martensite or austenite.

The shock-induced physical and chemical effects and features in the Yanzhuang meteorite are also presented in the following aspects:

(1) Natural diaplectic olivine glass and diaplectic pyroxene glass were discovered for the first time in the naturally shocked Yanzhuang meteorite in 1992. The diaplectic olivine glass was identified by the stronger Raman frequencies at 1108 cm^{-1} and 1180 cm^{-1}, and the diaplectic pyroxene glass by the weak Raman frequencies at 816 ~ 840 cm^{-1}.

(2) As early as in 1992, high–pressure phase minerals including ringwoodite and majorite were found for the first time in H group chondrites. The ringwoodite in Yanzhuang chondrite occurs in two different forms: the first is allotriomorphic granular ringwoodite which nucleated and crystallized from diaplectic olivine glass, and the second is euhedral ringwoodite which crystallized from shock–induced silicate melt. It was found that back transformation from spinel (γ –phase) to modified spinel (β –phase) , and to olivine took place for more than 90% ringwoodite after the unloading of shock wave. Majorite in Yanzhuang nucleated and crystallized from diaplectic pyroxene glass. It was also damaged or transformed back to pyroxene after the unloading of shock wave.

(3) It was found that the shock wave can cause the structural deformation and structure reorganization of some pyroxene and its high–pressure phase. In addition to itself two–bridging Si–O tetrahedral chain structure, some complicated combination of Si–O tetrahedral groups, including the Si–O tetrahedral with one or four non–bridging oxygen, as well as fully polymerized Si–O tetrahedral, were partially produced in some shocked "pyroxenes" .

(4) Condensation of shock–induced crystals of olivine, pyroxene, and troilite, as well as whiskers and needles of FeNi metal were found in holes or fractures in the Yanzhuang chondrite. A vapor growth model for FeNi metal whiskers and needles was proposed on the basis of their micro–morphological features.

(5) Extremely large eutectic FeNi + FeS blobs up to 1.1 cm in length were observed in shock–induced silicate melt. In melt veins, three micro–structural and compositional zones and the new "step–type" distribution pattern of Ni content in FeNi metal dendrites in eutectic blobs were discovered, namely, the zone A of FeNi metal is composed of microlites and non–crystalline phase firstly solidified in the episode of greater cooling speed, and subsequently, the zone B of FeNi metal is composed of coarser crystals crystallized due to the dropping cooling speed; and the zone C of FeNi metal is condensed at last from the remained liquid phase of metal. In contrast to the three–zone micro–structure of FeNi metal in melt veins, the FeNi metal dendrites in melt pockets, having greater volume of molten materials, only show two micro–structural zones, zone B and zone C. They occur in the symmetrical form of crust and nucleus. This implies that the FeNi metal solidified at lower cooling speed and in symmetrical heat radiation field.

(6) A specific tetra–concentric–ring growth structure was observed on the head of FeNi metal dendrites of various shapes. The development and growth of such growth structure are identical in three dimensional directions. This growth structure is characterized as being multilayered. The formation, propagation and interaction of tetra–concentric–ring growth structures in the same layer are responsible for the growth of dendrite tip and stem, while dendrite side–branches are grown up at the junction of interaction of coupled tetra–concentric–ring growth steps between the adjacent two layers. Once independent side–branches are formed, their stems, tips and side–branches will be developed in the same mechanism of the growth as the tetra–concentric–ring structures. The repetition of above–described process will result in the formation of an array of dendrite.

(7) An assemblage with FeNi metal, troilite, Fe–Mn–Na phosphates and Al–free chromite was identified in a large FeNi–FeS eutectic blob in the Yanzhuang shock–produced chondritic melt. A few Fe–Mn–Na phosphate globules have composition of Na–bearing graftonite $(Fe,Mn,Na)_3(PO_4)_2$, and the majority of them corresponds to two phosphate minerals: Mn–bearing galileiite $Na(Fe,Mn)_4(PO_4)_3$ and a possible new phosphate mineral of $Na_2(Fe,Mn)_{17}(PO_4)_{12}$ composition. The elements of P, Na and Mn in these minerals came from the dissociation of previous minerals, such as merrillite, plagioclase and chromite in chondrite. Chromite in this assemblage is Al–free which is quite different with that of chromite (Al_2O_3=7.98%) in chondritic mass. The contents of minor components in this recrystallized chromite, such as MgO, CaO, MnO, SiO_2, and TiO_2, are also markedly decreased than the chromite in chondrite.

(8) The results of instrumental neutron activation analysis show that a similarity in bulk composition between shock–induced whole–rock melt and unmelted chondritic rock of Yanzhuang, which suggests in situ melting and fast cooling of the materials in both melt veins and melt pockets. While the major element concentrations of olivine, pyroxene, FeNi metal and troilite remain unchanged, some trace elements were slightly redistributed between these phases. Ga is enriched in the metal; Co, Cr and Zn are enriched in the sulfide; Cr is enriched in olivine and pyroxene, and Ti is enriched in the plagioclase glass.

(9) LA–ICPMS analyses show the following element redistribution after shock melting of the Yanzhuang chondrite: ① The siderophile elements Fe, Ni and Co mainly concentrated in the FeNi metal blobs embedded in the whole–rock melt phase, while the elements Cr, V, Ti and Mn transferred into pyroxene crystallized from silicate melt to substitute Al^{3+}. ② The chalcophile elements Cu, Ga and Pb also concentrated in FeNi metal phase, while the volatile element Zn partly lost upon melting, but it mainly transferred into the micro–crystalline pyroxene and olivine crystallized from the silicate melt to substitute Fe^{2+}. ③ The lithophile elements Sc, Zr, Nb, and Ta basically enriched in the silicate melt phase, but the differentiation degree of Nb and Ta is low, and the Nb/Ta ratio of the FeNi metal phase is lower than the silicate melt phase in more than 1 times, indicating that the activization ability of Nb is higher than Ta upon high P–T melting. ④ The rare earth elements (REE) patterns of whole–rock melt and silicate melt phases hold the characteristic feature of Oddo–Harkins rule, and show the tendency of enrichment of light REE and depletion of heavy REE, but the FeNi metal phase displays depletion of light REE, and its total REE content is lower than the silicate melt phase in about 3 times. This indicates that REE, especially the light REE, are enriched in the silicate melt phase. ⑤ Platinum group elements are moved to FeNi–metal phase after shock melting.

(10) Quantitative micro–PIXE analysis of FeNi + FeS blobs on an etched section of the Yanzhuang meteorite shows that the core–crust microstructure of FeNi metal dendrite can be observed in Fe and Ni maps. The average composition of the metal core is Fe = 91.2% and Ni = 8.77 %, which is equivalent to martensite composition, and that of the metal crust is Fe = 85.1% and Ni = 14.3%, which is equivalent to γ–FeNi

(taenite) . The S exists in troilite (FeS) with the content of 46%. Cr in both metal core and crust is less than 200 μg/g, and in troilite is 600 ~ 1 300 μg/g. Cu, Zn and Se seem to distribute in troilite but Ge is in the metal core. About 200 μg/g Se is in the troilite and 70 μg/g Ge in the metal core.

(11) Two special thermo–luminescence (TL) phenomena were found in the Yanzhuang meteorite through the determination of the natural TL, annealed TL and induced TL by β–radiation: ① when the Yanzhuang sample was annealed at temperature up to 500℃, the TL peak induced by β–rays shifted to lower temperature with the increasing of irradiation dose; ② when the annealed temperature is greater than 600℃, the TL peak temperature of the annealed sample was higher than that of the unannealed sample. This implies that the shock effect could change the TL characteristics of a chondrite. The measured equivalent β–dose for the melted and unmelted parts are 9238 Gy and 25753 Gy, respectively, showing that the thermal event ages for the two phases in the Yanzhuang meteorite are not equal, and their thermal histories are not the same, either.

(12) It was found that the shock effects of four different phases in Yanzhuang, namely, shock melt and recrystallized phase (M) , very strongly shocked phase (S6) , strongly shocked phase (S5) , and moderately shocked phase (S4) , can be compared with those of the Jilin (H5) chondrite experimentally shock–loaded from 12 to 133 GPa. However, the P–T conditions for the typical shock effects observed in experimentally shock–loaded samples may not be consistent with those for the similar effects observed in naturally shocked meteorites. This is because the big difference in pressure retaining time between them.

The Yanzhuang chondrite was spalled off its parent body in a collision event between two asteroids at 2.6 Ma ago. The estimated speed of the impact was about 7 ~ 8 km/s. The shock peak pressure acted on Yanzhuang was estimated as >60 GPa and the shock peak temperature 2000℃. Based on the studies in the shock effects of rocks and minerals, it was assumed that the Yanzhuang chondrite is really a most heavily shocked ordinary H group chondrite ever found and it contains most abundant shock induced melt among all known shock–melt–bearing chondritic meteorites.

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