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Feng Huibin, Meng Fancong, Li Shengrong, et al. The genesis of zonal texture of chromites from the Qingshuiquan serpentinite in East Kunlun Mountains[J]. *Geology in China*, 2015, 42(3): 785–802(in Chinese with English abstract).

东昆仑清水泉蛇纹岩中铬铁矿环带成因

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摘要: 东昆仑造山带清水泉超基性岩已蚀变成蛇纹岩, 部分浸染状铬铁矿颗粒具有环带结构, 这将为研究铬铁矿形成后所经历的变质过程及其寄主岩体的构造演化提供可靠的信息。通过对铬铁矿进行显微结构观察和电子探针分析得出: 所研究铬铁矿的环带结构从核部到边缘依次为铝铬铁矿、高铁铬铁矿和铬磁铁矿, 被绿泥石所包裹。从铝铬铁矿到高铁铬铁矿, Cr_2O_3 , Al_2O_3 和 MgO 含量下降, Fe_2O_3 和 FeO 含量升高; $\text{Cr}^\#$, TiO_2 含量, YFe 值以及 Fe^{2+} 值明显具有升高的趋势, 而 $\text{Mg}^\#$ 值却急剧下降。以上变化规律表明本文所研究的铬铁矿经历了由高温到低温, 同时氧逸度上升的过程, 并伴随有蛇纹石化作用、热液流体以及区域变质作用等改造, 最终形成环带结构。此过程与铬铁矿寄主岩体经历的由地幔抬升至浅部地壳以及相关的变质作用过程相对应。

关键词: 东昆仑; 蛇纹岩; 铬铁矿; 环带结构

中图分类号: P618.3; P588.12⁺5 文献标志码: A 文章编号: 1000-3657(2015)03-0785-18

The genesis of zonal texture of chromites from the Qingshuiquan serpentinite in East Kunlun Mountains

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Abstract: The ultrabasic rocks in the Qingshuiquan area of Eastern Kunlun Mountains have been altered into serpentinite, in which the zonal texture of some chromites provides important information concerning the alteration and evolutionary process of the rocks. The result of electron microprobe analysis shows that the girdle of chromite is composed of three parts, i.e., aluminous-chromite, ferri-chromite and chrome-magnetite, from core to rim, respectively, and all of them were wrapped in chlorite. From the aluminous-chromite to the ferri-chromite, the Cr_2O_3 , Al_2O_3 , MgO and $\text{Mg}^\#$ values decrease, while the Fe_2O_3 , FeO , TiO_2 as well as $\text{Cr}^\#$ and YFe values increase. The authors hold that, along with the serpentinitization and regional metamorphism as well as hydrothermal fluid activity, the chromite went through a process in which the temperature was decreasing and the oxygen fugacity was increasing. And

收稿日期: 2014-11-01; 改回日期: 2014-12-01

基金项目: 国家自然科学基金(41272052)和中国地质调查局项目(1212010918003, 1212011120158, 12120114080101)联合资助。

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then the zonal texture was formed. This process corresponded to another one during which the host rock of the chromite moved upward from the mantle to the crust, accompanied by metamorphism.

Key words: East Kunlun Mountains; serpentinite; chromite; zonal texture

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1 引 言

铬铁矿作为副矿物存在于橄榄岩中,它相对于其他岩浆成因矿物更加稳定,对形成环境的变化更加敏感^[1-4]。根据铬铁矿形成时的物理化学条件,如温度,压力,氧逸度和部分熔融程度等,可以追溯寄主岩石成因及地幔特征^[1,5-12]。但是,值得注意的是,只有通过岩相学和化学成分等特点区分出来的原生铬铁矿才具有原始岩石成因指示意义^[1,5,7,13],而次生蚀变形成的铬铁矿特征可以为研究原生铬铁矿颗粒形成后所经历的变化过程提供依据,也为进一步讨论其寄主岩体的地质演化过程提供可靠资料。

东昆仑清水泉出露的超基性岩受到强烈的蛇纹石化作用而转变成蛇纹岩,其中的铬铁矿作为副矿物分布于蛇纹岩中^[14-19]。部分铬铁矿由于后期蛇纹石化作用,区域变质作用以及流体的影响而形成环带结构,由核部到边缘依次为铝铬铁矿、高铁铬铁矿和铬磁铁矿,它们被绿泥石所包裹,共同处于以蛇纹石为主的基质中。

铬铁矿环带结构的成因早已引起广大学者的注意,尤其是高铁铬铁矿作为最重要的组成部分更是受到了高度关注。高铁铬铁矿通常在英文文献中被称为“ferritchromite”或“ferritchromit”^[2,20-21],已被广泛的研究和报道于许多地区^[21-33]。高铁铬铁矿的形成被广泛认为与铬铁矿寄主岩体所经历的蛇纹石化作用^[25,34-35];绿泥石化作用^[10,22,36];绿片岩相一角闪岩相的低程度变质作用^[25-26,37]以及热液蚀变过程^[2,21,25,28,38-42]有关,但是高铁铬铁矿的产生一直是一个争论的话题,对于其成因存在多种意见,并且不能使用单一的过程来解释,所以还没有形成统一的观点。

清水泉铬铁矿环带结构的研究在前人的工作中并未得到重视,本文通过对东昆仑清水泉超基性岩(蛇纹岩)中铬铁矿的形态学和矿物化学的研究区分出原生和蚀变铬铁矿,并利用变质铬铁矿化学成

分推断其环带结构的成因,这将为铬铁矿及其寄主岩体所经历的地质动力学演化过程研究提供重要信息。

2 地质背景

东昆仑造山带西起新疆境内的阿牙克库木湖北岸,向东至清水泉及其以东吉日迈地区,长约1000 km,南北宽50~200 km,近东西向分布。以东昆中断裂带为界,将东昆仑分为昆北和昆南两部分,东昆仑造山带以北为柴达木盆地,以南为巴颜喀拉—松藩甘孜地体^[43-53](图1)。

昆北地区最老岩系为中元古代金水口群,由各类片岩,片麻岩,大理岩及少量石英岩组成,原岩是一套深海相砂泥质碎屑岩和中—基性火山岩,上被新元古界冰沟群滨海—浅海相碎屑岩及碳酸盐岩不整合覆盖^[44],金水口群遭受早古生代角闪岩相至麻粒岩相变质作用^[44,47,54-55];早古生代纳赤台群遭受绿片岩相变质以及花岗岩侵入破坏^[43,45];最晚为泥盆世契盖苏群^[47]。昆北地体还分布有早古生代花岗岩以及三叠纪岛弧岩浆性质花岗岩^[45],后者对前者进行了强烈的改造。

昆南最老岩系为元古宙苦海群和万宝沟群,分别经历了角闪岩相和绿片岩相变质作用^[43,56];之后是早古生代的纳赤台群,仅经历低级变质作用^[43];造山作用晚期,形成泥盆纪牦牛山组磨拉石建造^[56-58]。昆南“软基底”^[43]之上为一套产于被动陆缘环境的早古生代深海碎屑岩和基性火山岩^[44],整个地体被早古生代花岗岩所侵入,并伴随有大量的三叠纪碰撞型花岗岩的侵入^[45]。印支期花岗岩的侵位对前期构造进行了强烈的改造,所有老地层中均叠加有清楚的印支期构造变形遗迹^[14]。

清水泉超基性岩体位于都兰县香日德镇东南约60 km,地理坐标为: E: 97°30′~99°00′ N: 35°30′~35°50′,海拔约3600 m(图2)。清水泉超基性岩体呈近NWW向延伸,围岩是中元古代白沙河岩群

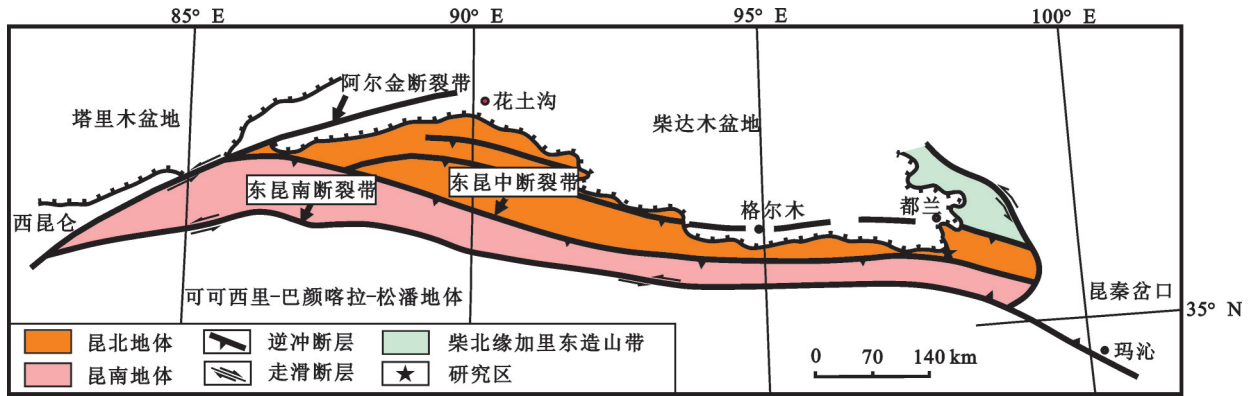


图1 东昆仑造山带大地构造位置图(据参考文献[52]修改)

Fig. 1 Geotectonic location of East Kunlun orogenic belt (modified after reference [52])

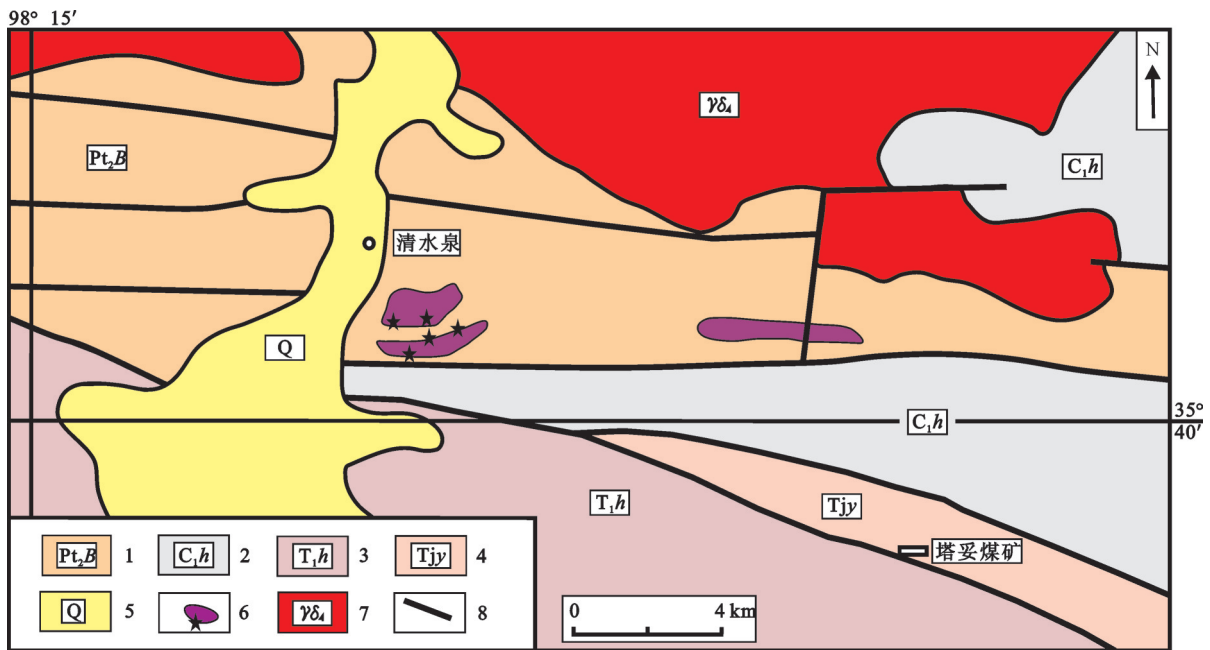


图2 清水泉地区地质简图(据参考文献[59]修改)

1—中元古界白沙河群; 2—早石炭世哈拉郭勒组; 3—早三叠世洪水川群; 4—三叠系—侏罗系羊曲组; 5—第四系; 6—镁铁—超镁铁质岩及采样点; 7—印支期花岗闪长岩体; 8—断层

Fig. 2 Geological map of the Qingshuiquan area (modified after reference [59])

1—Mesoproterozoic Baishahe Group; 2—Early Carboniferous Halaguole Formation; 3—Early Triassic Hongshuichuan Group; 4—Triassic—Jurassic Yangqu Formation; 5—Quaternary; 6—Mafic—ultramafic rock and sampling location; 7—Indosinian granodiorite; 8—Fault

(Pt₂B), 围岩岩石组合为: 斜长角闪岩, 浅粒岩, 变粒岩, 大理岩, 麻粒岩, 片麻岩等, 其变质程度为角闪岩相—麻粒岩相, 呈东西向高角度构造变形。辉长岩, 辉绿岩多以岩脉岩墙等形式局部出现, 穿插于大理岩和蛇纹岩中。

3 研究方法

本文主要针对蛇纹岩中所含尖晶石族矿物进

行形态特征和矿物化学等方面工作, 所测试的铬铁矿样品均来自蛇纹岩, 磨制探针薄片后挑选部分具有环带结构铬铁矿颗粒的样品进行电子探针分析, 此工作主要是在中国地质科学院地质研究所电子探针(EPMA)实验室完成的, 实验仪器型号为JXA-8100, 工作加速电压为15 kV, 电流为 2.00×10^{-8} A, 束斑为5 μm。应用AX软件和Geokit软件^[60]等进行数据处理, 基于尖晶石化学计量法(AB₂O₄)的软件程序

计算全部阳离子数量,并将全铁含量区分为 Fe^{2+} 和 Fe^{3+} 。本文所用矿物缩写依据沈其韩^[61]。

4 样品特征

清水泉超基性岩大多已蚀变为蛇纹岩,主要以岩块产出(图2),呈条带状构造(图3-a~b),推测为受到区域变质作用而成。蛇纹岩零散出露于清水泉河东地区,近W—E方向延伸,其围岩主要是大理岩、浅色变粒岩和片麻岩,有辉长岩/辉绿岩脉穿插于大理岩和蛇纹岩中。蛇纹岩为灰黑—灰绿色,风化破碎严重,其中的尖晶石族矿物呈浸染状(图3-c)和条带状(图3-d)出现,条带宽0.5~1.5 cm,多不平整且延伸较短。在手标本中无法区分铬铁矿和磁铁矿,二者在蛇纹岩中所占比重之和<1%。

显微观察和电子探针结果显示蛇纹岩中所包含的矿物主要有铬铁矿,磁铁矿,蛇纹石,绿泥石,碳酸盐类矿物(主要是菱镁矿)等。蛇纹岩中铬铁矿含量<1%,粒径为0.3~2 mm,个别可达到3 mm,单偏光下呈浅红色、暗红色、红褐色和黑色等。部分铬铁矿具有明显的环带结构(图4-a、c、f~g、i),中部颜色较浅(浅红色),显示其富Al贫Fe的特性,而边缘为黑—黑红色,显示其富Fe的特性,在背散射图像中,边缘相对于核部具有较低的灰度,也反映出Fe元素含量的升高,环带与核部具有明显的光学边界^[28, 34-35, 39, 62]。部分铬铁矿内部还存在裂隙和包体(图4-c、e~f);磁铁矿多呈细小的黑色颗粒存在于蛇纹石间隙以及铬铁矿内部裂隙中(图3-g,图4-e),含量<1%,还有部分磁铁矿围绕铬铁矿颗粒边缘分布(图4-b、g~h);蛇纹石在蛇纹岩中所占比重达95%,蛇纹石种类未做精确测定,主要呈网状结构(0.4~0.8 mm)(图3-g~h),中心充填有蛇纹石和碳酸盐矿物,由此推测原岩可能为残碎斑状结构,其原始矿物可能是具等粒状或残碎斑状的橄榄石;绿泥石在正交镜下具有异常干涉色(墨水蓝色),含量较少且分布不均匀,少量呈细长条状分布于铬铁矿颗粒之间(图3-e),多数呈环带状包裹铬铁矿颗粒(图4-i~j);碳酸盐类矿物主要呈灰—褐色不规则集合体分布于蛇纹石颗粒边缘(图3-f),部分充填于蛇纹石网状结构中心,绿泥石与碳酸盐类矿物总量约为2%。

根据显微镜下铬铁矿颗粒的形态特征将浸染状铬铁矿分为以下3类:

第一类:颗粒完整,半自形—自形,颗粒边缘较平滑,内部无包体和裂隙存在,无环带结构,部分颗粒周围分布有一薄层黑色磁铁矿颗粒(图4-b、h);

第二类:颗粒破裂,他形,颗粒边缘不规则,内部可见包裹体以及少量较窄裂隙,无环带结构,部分颗粒周围分布少量细小黑色磁铁矿颗粒(图4-e);

第三类:颗粒破碎,呈不规则状或孤岛状,个别可见矿物包裹体,且存在多组多方向裂隙,具环带结构,核部形状不规则,外侧环带厚度变化较大(50~200 μm)且形状多变,呈港湾状(图4-a、c、f~g、i)。

环带状铬铁矿在显微镜下呈破碎的,不规则的港湾状(图4-a、c),并有无规律的裂隙穿过铬铁矿颗粒(图4-c、f),表明此类铬铁矿经过了后期变质作用的改造,其环带结构是后期蚀变改造形成的,具次生成因;环带状铬铁矿核部的边缘表现出不平整的锯齿状形态,且具有与其所在的完整铬铁矿颗粒相近的形状特征(图4-g),因此认为环带状铬铁矿核部为原始铬铁矿经蚀变作用后所残留的部分,具原生成因。

环带铬铁矿主要存在于网状蛇纹石基质中,蛇纹石网状结构可分为变形与未变形2种(图3-g~h)。未变形的网状结构单元为多边形,包括核部和边缘,边缘通常为纤维状蛇纹石,近于垂直网状结构边界,而核部常为各向同性(较老文献中称为“胶蛇纹石”)^[63],有时也见细粒状结构。变形的网状结构单元是因为受到变形作用的影响,其形状多为透镜状,此类网状结构单元的边缘要大于核部,甚至不存在核部。网状结构是出现在许多蛇纹岩中常见的退化结构^[63-65]。

5 测试结果

铬铁矿(FeCr_2O_4)属于尖晶石族矿物($(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4$),结构中普遍存在Mg与 Fe^{2+} 之间,以及Cr、Al和 Fe^{3+} 之间的类质同象替代^[5],因此铬铁矿的化学成分可以在一定的范围内发生变化。根据铬铁矿探针数据(表1~2)可清晰区分出核部与边缘之间成分的明显差异,但各部分化学成分在同一颗粒中或不同颗粒间是比较均匀的。核部 Cr_2O_3 含量为38.24%~44.34%, Al_2O_3 含量为24.18%~29.55%,FeO含量为15.18%~20.32%,而 Fe_2O_3 含量为0.85%~2.48%,由核部低Cr(<50.00%)低Al、Fe(<30.00%)的

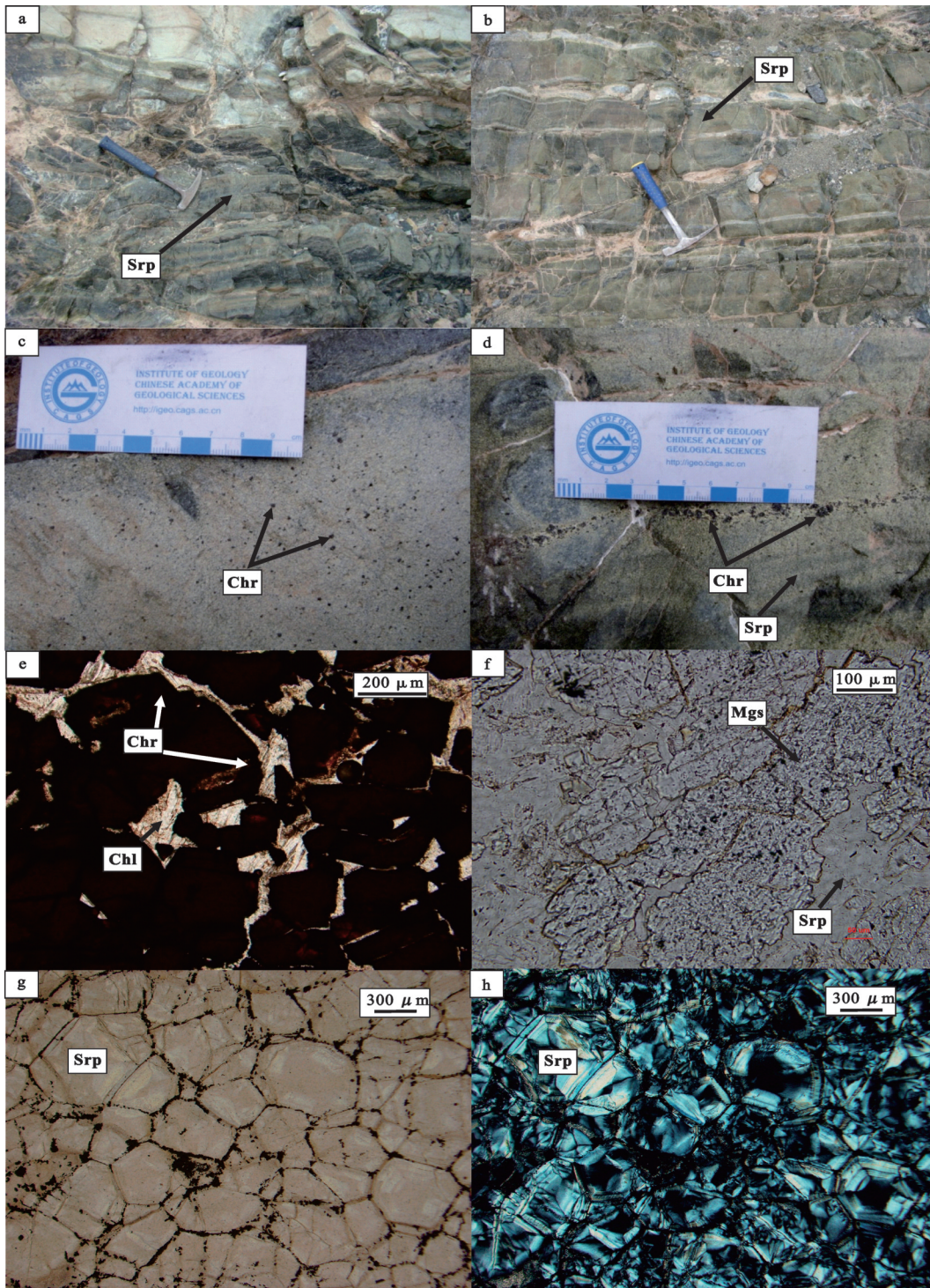


图3 蛇纹岩和铬铁矿野外产状及镜下特征

a, b—条带状蛇纹岩; c—浸染状铬铁矿; d—条带状铬铁矿; e—条带状铬铁矿及颗粒间分布的绿泥石(单偏光); f—蛇纹石中分布的碳酸盐矿物(菱镁矿)(单偏光); g, h—蛇纹岩的网状结构, 其中主要充填碳酸盐和蛇纹石(g—单偏光; h—正交偏光); Srp—蛇纹石; Chr—铬铁矿; Chl—绿泥石; Mgs—菱镁矿

Fig. 3 Field photograph and microscopic characteristics of serpentinite and chromites

a, b—Banded serpentinite; c—Disseminated chromite; d—Banded chromite; e—Banded chromite and chlorite in the gap (plainlight); f—Carbonate mineral (magnesite) in the serpentine (plainlight); g, h—Stockwork structure of serpentinite, filled with carbonate and serpentinite (g—plainlight; h—crossed nicols); Srp—Serpentine; Chr—Chromite; Chl—Chlorite; Mgs—Magnesite

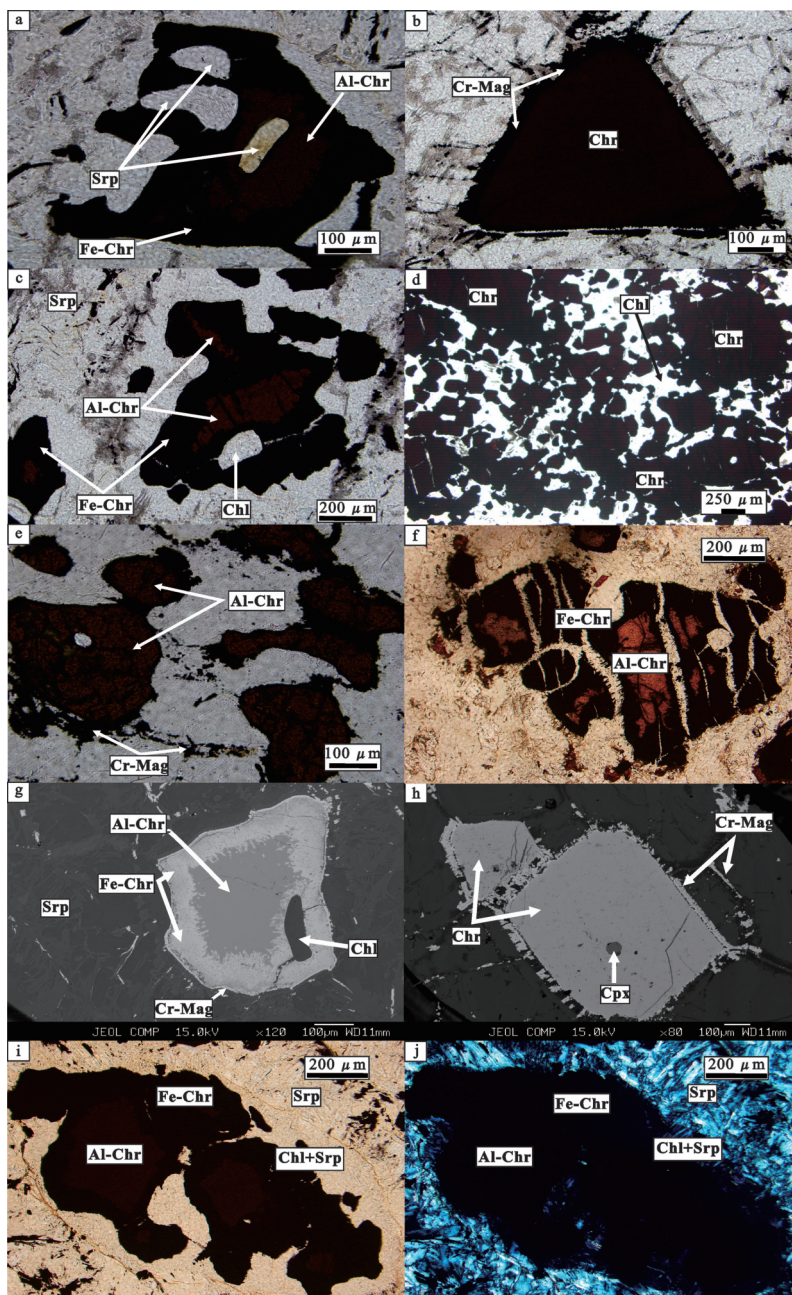


图4 清水泉铬铁矿形态结构特征

a—具有高铁铬铁矿环带的不规则状铝铬铁矿,且含有蛇纹石包体;b—自形铬铁矿;c—具有环带的不规则状铬铁矿;d—条带状铬铁矿及颗粒间分布的绿泥石;e—无环带的不规则铬铁矿;f—具有环带结构的破碎铬铁矿颗粒,可见原始的颗粒界线;g—具有高铁铬铁矿环带的不规则状铝铬铁矿,且高铁铬铁矿中含有绿泥石包体;h—自形的,含有Cpx包体的铬铁矿,边缘出现少量磁铁矿;i,j—完整的环带结构;Srp—蛇纹石;Al-Chr—铝铬铁矿;Fe-Chr—高铁铬铁矿;Chr—铬铁矿;Chl—绿泥石;Cr-Mag—铬磁铁矿;Cpx—单斜辉石(a~f,i为单偏光;g~h为背散射图片;j为正交偏光)

Fig. 4 Photomicrographs and back-scattered electron images showing typical textures of chromites

a-Irregular aluminochromite with serpentine inclusions, surrounded by ferri-chromite; b-Euhedral chromite; c-Zoned irregular chromite; d-Banded chromite and chlorite in the gap; e-Irregular chromite; f-Zoned irregular chromite composed of several parts, with its outlines still recognizable; g-Irregular aluminochromite surrounded by ferri-chromite, and chlorite appearing in the ferri-chromite as an inclusion; h-Euhedral chromite with clinopyroxene inclusions, surrounded by a spot of magnetite; i, j-Complete zonal texture; Srp-Serpentine; Al-Chr-Aluminochromite; Fe-Chr-Ferri-chromite; Chr-Chromite; Chl-Chlorite; Cr-Mag-Chromium magnetite; Cpx-Clinopyroxene (a~f, i-Plainlight; g~h-Backscattered electron image; j-Crossed nicols)

表1 代表性铝铬铁矿主量元素(%)电子探针分析结果
Table 1 Representative composition of aluminochromites from Qingshuiquan serpentinite(%)

分析项目	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14
	-1.3-36	-1.3-41	-1.6(2)-51	-1.6(2)-52	-3.1-7	-3.1-13	-3.1-18	-3.1-24
	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]	铝铬铁矿 [#]
SiO ₂	0.02	0.01	0.01	0.02	0.10	0.04	0.09	0.06
TiO ₂	0.00	0.02	0.00	0.09	0.02	0.00	0.05	0.01
Al ₂ O ₃	29.55	28.01	28.52	28.47	24.18	26.00	26.51	25.61
Cr ₂ O ₃	39.08	40.77	39.14	38.24	44.34	43.17	40.83	42.56
Fe ₂ O ₃	2.09	1.89	2.48	2.29	1.20	0.85	2.04	1.09
FeO	15.18	15.66	17.35	18.89	17.06	17.54	18.69	20.32
MnO	0.30	0.29	0.29	0.35	0.32	0.27	0.33	0.37
MgO	13.83	13.42	12.36	11.28	11.84	11.95	11.32	10.16
CaO	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01
Na ₂ O	0.02	0.00	0.00	0.00	0.05	0.01	0.00	0.00
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.02	0.00	0.00
NiO	0.07	0.10	0.13	0.11	0.06	0.06	0.06	0.02
Totals	100.10	100.09	100.16	99.63	99.11	99.85	99.86	100.19
Oxygens	4	4	4	4	4	4	4	4
Si	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	1.04	0.99	1.01	1.02	0.88	0.94	0.96	0.93
Cr	0.92	0.97	0.93	0.92	1.09	1.04	0.99	1.04
Fe ³⁺	0.05	0.04	0.06	0.05	0.03	0.02	0.05	0.03
Fe ²⁺	0.38	0.39	0.44	0.48	0.44	0.45	0.48	0.53
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	0.61	0.60	0.55	0.51	0.55	0.54	0.52	0.47
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	3	3	3	3	3	3	3	3
Cr [#]	0.47	0.49	0.48	0.47	0.55	0.53	0.51	0.53
Mg [#]	0.62	0.60	0.56	0.52	0.55	0.55	0.52	0.47
YFe	0.02	0.02	0.03	0.03	0.01	0.01	0.02	0.01
Fe ^{2+#}	0.38	0.40	0.44	0.48	0.45	0.45	0.48	0.53

注: Cr[#]= Cr/(Cr+Al); Mg[#]= Mg/(Mg+Fe²⁺); YFe= Fe³⁺/(Cr+Al+Fe³⁺); Fe^{2+#}=Fe²⁺/(Mg+Fe²⁺); Fe²⁺为利用AX软件,由铬尖晶石结构式计算所获得。

性质,将其命名为铝铬铁矿;边部 Cr₂O₃ 含量为 26.46%~37.05%, Al₂O₃ 含量为 0.38%~0.98%, FeO 含量为 27.14%~31.18%, 而 Fe₂O₃ 含量为 23.08%~

40.41%, 由其高 FeO*(54.00%~89.00%)的特征可归属于高铁铬铁矿;分布在环带铬铁矿颗粒周围的细粒黑色矿物,其 FeO 含量约为 30.00%, 而 Fe₂O₃ 含量

表2 代表性高铁铬铁矿与磁铁矿主量元素(%)电子探针分析结果

Table 2 Representative composition of ferri-chromites and magnetites from Qingshuiquan serpentinite(%)								
分析项目	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14	QM09-14
	-1.3-35	-1.3-40	-1.3-47	-3.1-30	-1.6(2)-47	-1.6(2)-56	-4.3-71	-4.3-83
	高铁铬铁矿 [~]	高铁铬铁矿 [~]	高铁铬铁矿 [~]	高铁铬铁矿 [~]	高铁铬铁矿 [~]	高铁铬铁矿 [~]	铬磁铁矿 [~]	铬磁铁矿 [~]
SiO ₂	0.20	0.28	0.27	0.10	0.04	0.03	0.15	0.07
TiO ₂	0.16	0.19	0.20	0.10	0.11	0.52	0.03	0.02
Al ₂ O ₃	0.38	0.64	0.98	0.71	0.27	0.26	0.03	0.00
Cr ₂ O ₃	33.18	33.47	33.71	37.05	28.37	26.46	3.88	1.77
Fe ₂ O ₃	34.63	33.61	33.56	23.08	39.44	40.41	64.97	65.65
FeO	27.27	27.14	28.65	28.44	30.66	31.18	31.14	28.83
MnO	2.69	2.53	1.53	0.70	0.27	0.19	0.07	0.22
MgO	1.29	1.47	1.41	2.21	0.28	0.20	0.06	0.71
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.01	0.00	0.04	0.04	0.03	0.03	0.04
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
NiO	0.28	0.28	0.31	0.15	0.16	0.10	0.01	1.92
Totals	99.81	99.32	100.30	98.86	99.48	99.27	100.36	97.31
Oxygens	4	4	4	4	4	4	4	4
Si	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00
Ti	0.01	0.01	0.01	0.00	0.00	0.02	0.00	0.00
Al	0.02	0.03	0.04	0.30	0.01	0.01	0.00	0.00
Cr	0.98	0.99	0.99	1.06	0.85	0.80	0.12	0.06
Fe ³⁺	0.98	0.95	0.94	0.63	1.13	1.16	1.87	1.94
Fe ²⁺	0.86	0.85	0.89	0.86	0.98	1.00	1.00	0.95
Mn	0.09	0.08	0.05	0.02	0.01	0.01	0.00	0.01
Mg	0.07	0.08	0.08	0.12	0.02	0.01	0.00	0.04
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	3	3	3	3	3	3	3	3
Cr [#]	0.98	0.97	0.96	0.78	0.99	0.99	0.98	1.00
Mg [#]	0.08	0.09	0.08	0.12	0.02	0.01	0.01	0.04
YFe	0.49	0.48	0.48	0.32	0.57	0.59	0.94	0.97
Fe ^{2+#}	0.92	0.91	0.92	0.88	0.98	0.99	0.99	0.96

约为65.00%，Cr₂O₃含量约为3.00%，由此认为其应属于铬磁铁矿。根据铬铁矿分类图(图5)的判断结果与上述分析一致。

根据铬铁矿电子探针数据可看出各种氧化物的含量从铝铬铁矿到高铁铬铁矿的变化(图6):

Al₂O₃和MgO含量下降, Fe₂O₃和FeO含量升高, 而Cr₂O₃含量显示轻微的下降。此外, 由铬铁矿各部分特征值分布范围(表3)可以看出按照铝铬铁矿—高铁铬铁矿(即从核部到边部)的顺序, Cr[#]明显具有升高的趋势; Mg[#]值却急剧下降; TiO₂含量, YFe值以及

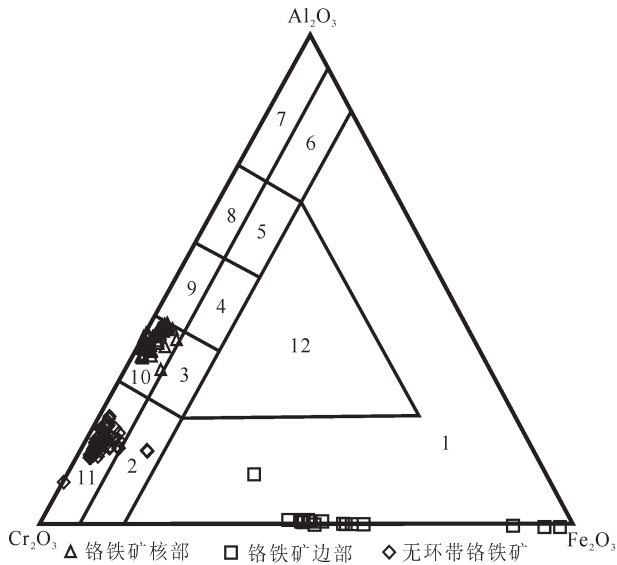


图5 铬铁矿分类图(据参考文献[66]修改)

1—高铁铬铁矿; 2—富铁铬铁矿; 3—富铁铝铬铁矿; 4—富铁富铬尖晶石; 5—富铁铝富铬尖晶石; 6—富铁铝尖晶石; 7—铬尖晶石; 8—铝富铬尖晶石; 9—富铬尖晶石; 10—铝铬铁矿; 11—铬铁矿; 12—高铁富铬尖晶石

Fig. 5 Classification of chromites (modified after reference [66])

1—Ferri-chromite; 2—Ferro-chromite; 3—Ferro-alumochromite; 4—Ferro-chromopicitote; 5—Ferro-alumopicitote; 6—Ferropicitote; 7—Picitote; 8—Alumopicitote; 9—Chromopicitote; 10—Alumochromite; 11—Chromite; 12—Ferri-chromopicitote

Fe^{2+} 值也显示出明显升高的趋势。

6 讨论

完整的铬铁矿环带结构(从核部到边缘)由以下几部分组成: 原始铬铁矿残留, 高铁铬铁矿和磁铁矿, 它们被绿泥石带所包裹, 共同处于以蛇纹石为主的基质中。环带结构各部分的化学组成以及接触关系是相互关联的, 各部分的形成与原始铬铁矿变化密切相关。

6.1 高铁铬铁矿

高铁铬铁矿 (ferrian chromite/ferritchromite/ferritchromit)是铬铁矿环带结构中最重要的一部分, 其概念第一次是用于形容位于蛇纹岩中分散的铬铁矿颗粒边缘的矿物, 典型的高铁铬铁矿与其包围的中心铬铁矿相比, 以相对富Fe为特征, 有时富Ni、Co、Ti、Mn和Zn, 而相对亏损Al和Mg^[20, 67]。后来就将铬铁矿蚀变产生的富Fe边缘称为高铁铬铁矿^[20, 22-25, 28, 39, 68-69], 其组成可表示为 $(Fe^{2+}, Fe^{3+}, Mg)[Cr, Fe^{3+}, Fe^{2+}, Al]_2O_4$ 。

由本文中铬铁矿成分的变化(图7)可以看出原始的铬铁矿核部沿着Cr—Al连线分布, 而高铁铬铁矿则沿着Cr—Fe³⁺的连线分布, 反映出Al₂O₃和Cr₂O₃的丢失以及Fe₂O₃含量的上升。

高铁铬铁矿成因的主要观点如下:

(1) 增生形成

高铁铬铁矿可作为以原始铬铁矿为核的增生产物。在蛇纹石化作用过程中, Cr、Fe和其他阳离子从原始的硅酸盐矿物中释放出来并进入流体, 导致过量的Cr和Fe存在于铬铁矿边缘, 进而形成高铁铬铁矿^[22-23, 35, 39]; 也可能是核部铬铁矿的阳离子外移并沉淀形成高铁铬铁矿^[67, 70]。

(2) 变质形成

多数人认为高铁铬铁矿是在区域变质作用过程中形成^[2, 25, 28, 31, 36, 71-73]。在蛇纹石化作用过程中主要产生磁铁矿, 随后变质作用上升至绿帘石—角闪石相, 原始铬铁矿与周围磁铁矿在进变质作用过程中反应形成高铁铬铁矿^[23, 25, 28, 74]; 也可能是原始铬铁矿与寄主岩石中绿泥石变质反应的产物^[40, 75]; 或者是受到与蛇纹石化作用相关的低温热液蚀变影响^[32, 42, 67, 76-78], 在含水条件下的进变质作用过程中形成^[31]; 抑或是在含水的氧化条件下, 退化产生高铁铬铁矿和绿泥石^[65], 即铬铁矿与蛇纹石反应的结果^[79]。此外, 还有人认为高铁铬铁矿是低压低温的退变质作用产物^[41], 受到了低—中级变质作用(达到低角闪岩相)的影响^[2, 3, 27, 80-83], 因此将高铁铬铁矿的形成归因于绿片岩相—低角闪岩相的转变^[33, 73]。

(3) 残留产物

在蛇纹石化作用过程中, Mg和Al从原始铬铁矿中释放出来形成相邻的绿泥石, 残留部分相对富集Fe和Cr, 形成高铁铬铁矿^[22]。

(4) 流体或岩浆蚀变

尘点状的磁铁矿说明蚀变的过程中富Fe流体的参与, 此流体渗透进入原始铬铁矿^[28, 67]并利用流体中的Fe置换铬铁矿中的Al, 从而使铬铁矿中的Al流失掉, 因此在反应边形成富Fe的高铁铬铁矿边缘^[65, 84]; 或者与岩浆蚀变作用有关^[25, 85-86]。

(5) 铬铁矿的出溶作用

温压等物理条件的变化导致铬铁矿物理形态的改变^[87]。

铬铁矿的组成和稳定性不仅依赖于体积组分、

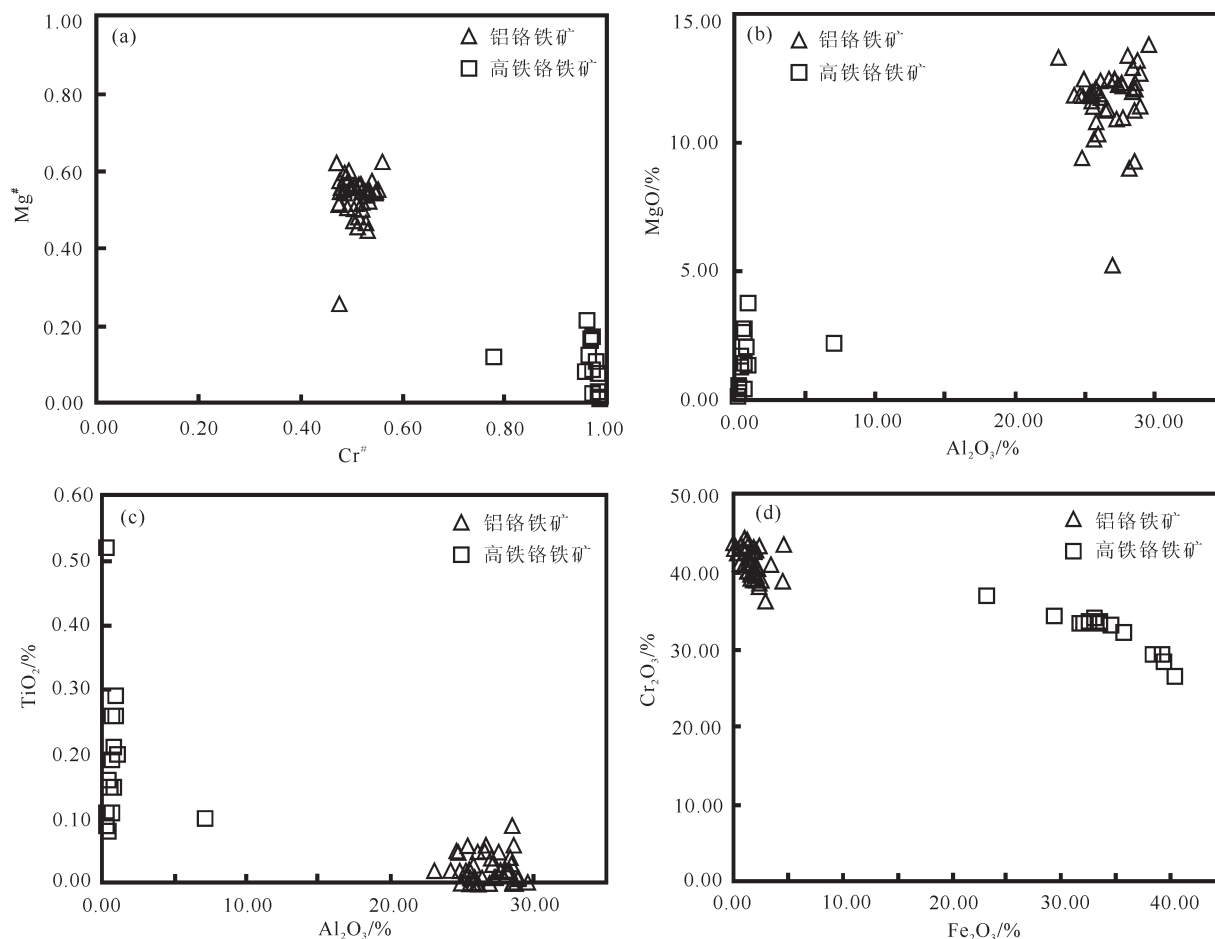


图6 铬铁矿成分变化趋势图

a—Cr[#]—Mg[#]图解; b—Al₂O₃—MgO图解; c—Al₂O₃—TiO₂图解; d—Fe₂O₃—Cr₂O₃图解

Fig.6 Variation trend of chromites composition

a—Composition of chromites in the Cr[#]—Mg[#] binary diagram; b—Composition of chromites in the Al₂O₃—MgO binary diagram; c—Composition of chromites in the Al₂O₃—TiO₂ binary diagram; d—Composition of chromites in the Fe₂O₃—Cr₂O₃ binary diagram

表3 铬铁矿特征值分布范围

Table 3 The eigenvalue range of chromites

特征值类别	铝铬铁矿	高铁铬铁矿
Cr [#]	0.47~0.56	0.78~0.99
Mg [#]	0.45~0.62	0.01~0.22
TiO ₂ /%	0.00~0.01	0.08~0.29
YFe	0.00~0.05	0.32~0.59
Fe ^{2+#}	0.38~0.55	0.74~0.99

压力和温度,还依赖于氧逸度^[88],随着氧逸度的升高,铬铁矿变得富Fe³⁺而贫Mg^[6, 10, 89]。在铬铁矿的环带结构中,边缘相对富Fe,贫Al和Mg,核部则相反。Fe²⁺和Fe³⁺在边缘高铁铬铁矿中的含量与核部

铝铬铁矿相比略有增加(表2),Fe³⁺/Fe²⁺值也升高,由Fe³⁺/(Fe²⁺+Fe³⁺)变化(图8)也可以看出其值在边缘高铁铬铁矿中升高的趋势(图8),由Fe³⁺/Fe²⁺,Fe³⁺/(Fe³⁺+Fe²⁺)值与氧逸度之间存在的正相关关系^[6, 22, 24, 90]推断边缘高铁铬铁矿产生时环境氧逸度相对于其核部铝铬铁矿形成时略有升高。高氧化条件有助于铬铁矿与蛇纹石反应^[21, 65]。因此认为原始铬铁矿形成高铁铬铁矿边缘是在氧化条件下,此蚀变应该发生于低温的角闪岩相变质作用过程中^[21, 83]。

火成岩中的铬铁矿组成受到熔体的组成,结晶作用压力和地幔源区的熔融程度的影响^[1, 5, 7, 91-92],而变质岩的铬铁矿组成则与变质程度有关^[2-3, 74, 76, 83-84, 87, 93]。此处高铁铬铁矿基本上位于低角闪岩相变质区域的

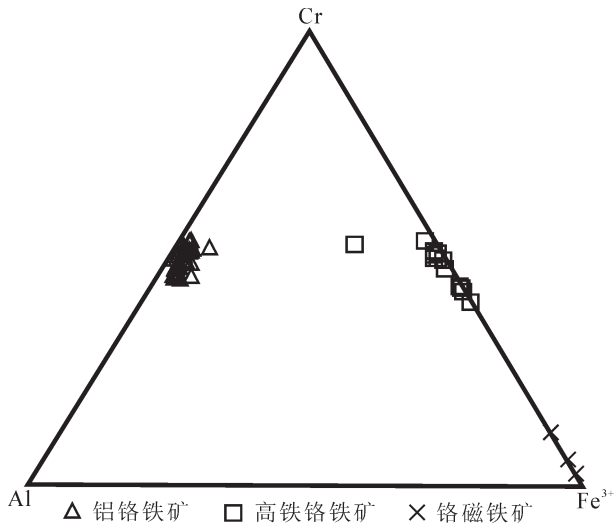


图7 Al-Cr-Fe³⁺铬铁矿环带成分变化图
Fig.7 Composition variation of zoned chromites in the Al-Cr-Fe³⁺ diagram

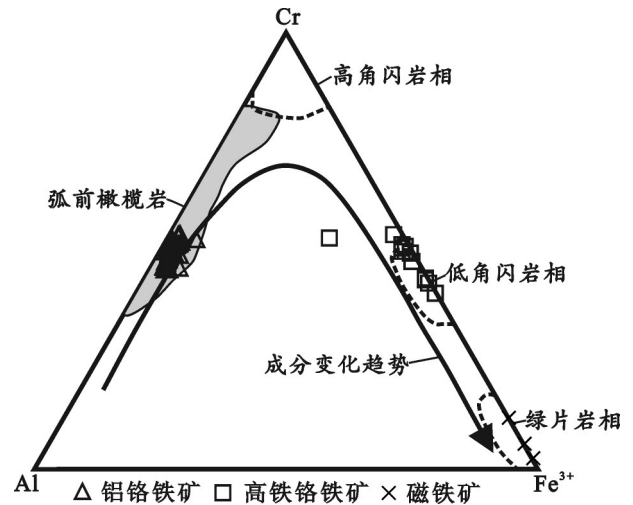


图9 铬铁矿变质程度Cr-Al-Fe³⁺三角图(据参考文献[94]修改)
Fig.9 Al-Cr-Fe³⁺ trivalent cation diagram showing degree of metamorphism of chromite (modified after reference [94])

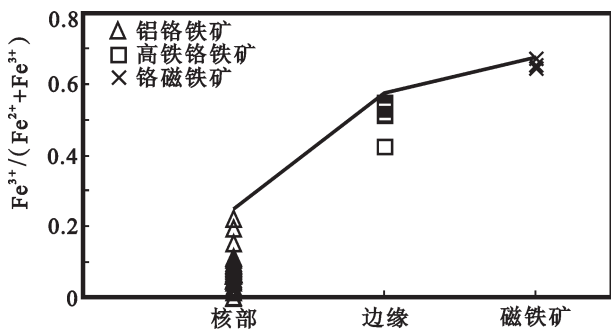


图8 铬铁矿颗粒中Fe³⁺/(Fe²⁺+Fe³⁺)变化趋势图
Fig.8 Fe³⁺/(Fe²⁺+Fe³⁺) trends of chromite crystals

边缘位置(图9),其稳定温度范围在500~600 °C(图10)。前人也曾利用地球化学证据证明高铁铬铁矿边缘(Fe³⁺>0.50)通常出现在超镁铁质岩石中的角闪岩相岩层中^[33],与500~600 °C的变质作用相一致,为绿片岩相至低角闪岩相变质^[95]。

通常认为岩浆结晶分异产生的铬铁矿从核部到边缘会显示出Cr[#]降低, Mg[#]升高的现象^[12],而本文所研究的铬铁矿却显示出从核部到边缘Cr[#]升高, Mg[#]降低的趋势,所以认为此处铬铁矿环带的产生不是岩浆结晶分异的结果。

由高铁铬铁矿的形态特征可知铬铁矿核部和蚀变的高铁铬铁矿边缘共同显示原始的铬铁矿形状(图4-g);铬铁矿核部边缘呈锯齿状(图4-g);环带

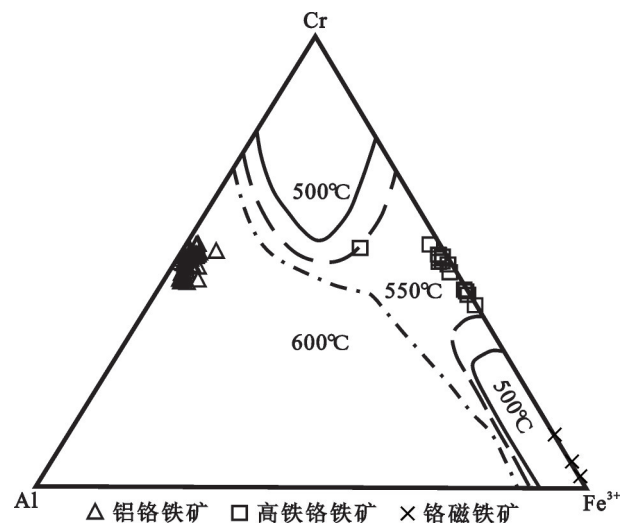


图10 与Fo₉₀橄榄石平衡的铬尖晶石稳定性判别图(据参考文献[28]修改)
Fig.10 Spinel stability distinguished by spinels in equilibrium with Fo₉₀ olivine (modified after reference [28])

状铬铁矿破碎分布,但基本保持了原始铬铁矿整体形态(图4-f)。由此推断高铁铬铁矿环带与原始铬铁矿分解有关,否定了高铁铬铁矿边缘是由于增生作用形成的观点。但是高铁铬铁矿的化学成分还受到外界流体的影响,例如未蚀变的铝铬铁矿核部的NiO含量很低(<0.15%)(表1),而高铁铬铁矿边缘可达到0.31%(表2),这是由于蛇纹石化作用过程中,橄榄石释放其中的Ni,随流体进入铬铁矿结构

内^[96]。Si在标准的铬铁矿结构中是不存在的,但是探针分析检测到少量的SiO₂(表2), Si出现在蚀变的颗粒边缘,推断存在于溶解元素(Al和Cr)的空位上,而SiO₂的来源可能是硅酸盐矿物或流体^[39]。

许多学者认为高铁铬铁矿是蛇纹石化作用的产物^[20, 22, 69, 97-99],但也有人认为它形成早于蛇纹石化作用或者形成于蛇纹石化作用之后的变质过程中^[74, 100-101]。在蛇纹石化过程中,铬铁矿晶格中的阳离子发生扩散,导致残留的铬铁矿中富集Fe和Cr^[22],但是铬铁矿作为一个晶体化学非常稳定的相,不太可能在如此低的温压条件下(例如蛇纹石化作用)参与化学成分的转化^[102-103]。此外,高铁铬铁矿不限于蛇纹岩中,在非蛇纹岩的岩石中也曾发现过,此类岩石在铬铁矿结晶后遭受了升温变化,例如玄武岩中的捕虏体和捕虏晶^[104-107]和一些变质沉积物^[100, 108],因此单独的蛇纹石化作用不足以产生高铁铬铁矿。

原始铬铁矿蚀变过程中,Al和Mg元素向外迁移,而Fe、Cr和Ti等元素均较稳定,成为高铁铬铁矿边缘的主要成分。大量的Al和Mg被带出后造成高铁铬铁矿中阳离子总数少于原始铬铁矿,因此需要原矿物中部分Fe²⁺被氧化成Fe³⁺,以及外部Fe³⁺的渗透进入高铁铬铁矿,以达到阳离子总电价平衡^[109]。所测铬铁矿的原始成分显示Fe₂O₃含量很低(<2.50%),不足以作为高铁铬铁矿中Fe³⁺的来源,因此认为高铁铬铁矿中的Fe³⁺是多来源的:原始铬铁矿中Mg、Al元素向外迁移,残留下来的Fe元素;硅酸盐矿物在蛇纹石化过程中释放Fe和Cr,被流体携带渗透进入铬铁矿^[23, 28, 110];原始铬铁矿与周围基质中的硅酸盐矿物和碳酸盐矿物进行Mg-Fe交换^[28]。

6.2 磁铁矿

尘点状磁铁矿是蛇纹石化作用的产物,橄榄石和辉石与含水流体反应形成蛇纹石和磁铁矿^[25, 111-119]。在蛇纹石化作用过程中,原始硅酸盐矿物中的Al和Cr相对比较稳定,而Fe从橄榄石和辉石中释放出来形成磁铁矿,细小的磁铁矿颗粒常形成不连续的串或行,沿着蛇纹石网状结构单元界线分布(图3-g),此类磁铁矿与蛇纹石应属于同期产物。

环带状磁铁矿分布于高铁铬铁矿外侧,包裹内部的铬铁矿颗粒。通常认为镁铁质岩中的磁铁矿大多含有相当大量的Al而不是Cr^[3, 120],但此处环带状磁铁矿中Cr₂O₃达到3.80%,而Al₂O₃最高仅为

0.03%,表明磁铁矿的另一种起源^[79]。铬铁矿作为蛇纹岩中Cr元素的主要载体,应该与磁铁矿中高Cr₂O₃含量的成因有关。有人认为在铬铁矿与周围绿泥石相互作用过程中,铬铁矿经过分解—平衡—再沉淀形成磁铁矿^[28, 67];或者认为磁铁矿形成并充填于铬铁矿边缘和裂缝是由于铬铁矿与共存的硅酸盐矿物(尤其是橄榄石)之间Mg和Fe²⁺交换的结果^[28, 121]。由此可见,环带状磁铁矿的形成是受到了铬铁矿分解的影响。

6.3 绿泥石

绿泥石少量分布在蛇纹石基质中,多数呈环带状包裹铬铁矿颗粒(图4-i-j)。高铁铬铁矿的形成导致Al、Mg和Cr向外扩散,为绿泥石环带的形成提供必要的物质来源^[22, 65, 76, 122-123],此过程发生在低温热液作用下,其形成所需要的SiO₂可能来自周围硅酸盐矿物蛇纹石化作用过程中的释放或者来自外来的富MgO和SiO₂的热液流体。

分布特征显示绿泥石与网状结构蛇纹石叠置在一起(图4-i-j),这就表明绿泥石的形成不是铬铁矿与富MgO、SiO₂流体反应的产物,而是铬铁矿与已经形成的蛇纹石反应的结果^[33, 96]。绿泥石围绕铬铁矿颗粒出现以及绿泥石与蛇纹石的叠置也证实高铁铬铁矿和绿泥石的形成晚于蛇纹石化作用。由此可见绿泥石的形成首先需要铬铁矿分解,部分元素向外迁移,随后影响外侧网状结构的蛇纹石,逐步转变成无序的绿泥石和蛇纹石。

由此可见在超镁铁质岩蛇纹石化作用之后,原始铬铁矿分解形成高铁铬铁矿边缘,残留富集Cr和Fe,而Al和Mg固定在共存的层状硅酸盐中(绿泥石和蛇纹石),过量的Al和蛇纹石的进一步反应形成绿泥石环带。

铬铁矿颗粒不同组合的出现代表了铬铁矿不同程度的变质。由铬铁矿显微特征可以看出,部分核部铝铬铁矿仅被稀疏的铬磁铁矿所包围,即表明还没有达到高铁铬铁矿形成的条件,应属于铬铁矿蚀变的前期。没有发现仅由高铁铬铁矿及铬磁铁矿组成的环带结构,这表明铬铁矿的蚀变还处于初期阶段,没有蚀变完全。

尖晶石族矿物作为副矿物,数量少,体积小,相对容易达到平衡,其作为等轴晶系矿物具有各向同性,即离子在各个方向上的扩散速率相同或者相

近, 所以其成分的分带也相应地记录了寄主岩体所经受的热事件^[24]。本文中所研究的铬铁矿经历了从高温到低温且氧逸度上升的变化过程, 以及蛇纹石化作用和区域变质作用等改造, 与其寄主橄榄岩经历的由地幔抬升至浅部地壳, 以及伴随的变质作用过程相对应。

7 结 论

铬铁矿环带结构形成的主要过程:

(1)原始的超镁铁质岩在低温低压的条件下发生蛇纹石化作用, 硅酸盐矿物转变成蛇纹石, 同时释放出部分Fe、Cr、Ni、Si、Al和Mg等元素, 这些元素进入与蛇纹石化作用同期的流体中, 部分Fe元素形成尘点状磁铁矿分布于蛇纹石网状结构单元的界线处, 此过程中副矿物铬铁矿的组成未发生明显变化。

(2)氧逸度的上升促进了元素的迁移, 铬铁矿晶格拉张, Mg、Al和少量的Cr向外迁移, 逐渐开始形成相对富Fe、Cr而贫Mg、Al的边缘部分, 此时处于500~600 °C的角闪岩相变质条件下, 外部流体中的阳离子(主要是Fe²⁺和Fe³⁺)为了保持电价平衡, 需要向铬铁矿边缘迁移聚集, 导致高铁铬铁矿环带的逐渐形成。

(3)过剩的Fe、Cr元素紧邻高铁铬铁矿边缘聚集, 形成了最外侧的磁铁矿环带部分, 此阶段处于绿片岩相变质条件下。

(4)高铁铬铁矿环带的形成改变了元素的分布状况, 进而影响到蛇纹石基质的结构和成分, 因此产生了绿泥石环带以及绿泥石与蛇纹石叠置的现象。

以上各个阶段组成一个连续的过程, 但相邻阶段之间不存在明显的时间界线, 可能存在时间上的重叠。整个环带结构的形成过程处于温度下降, 氧逸度升高的退变质作用(低角闪岩相—绿片岩相)条件下, 这与蛇纹石基质所显示的网状退化结构是一致的。由此可见, 本文中所研究的铬铁矿经历了从高温到低温, 同时氧逸度上升, 并伴随有蛇纹石化作用、热液流体以及区域变质作用等改造的过程, 最终形成环带结构, 与其寄主橄榄岩经历的由地幔抬升至浅部地壳以及相关的变质作用过程相对应。

致谢: 中国地质科学院地质研究所戎合老师帮助完成了矿物成分电子探针测试; 中国地质大学(北

京)及中国地质科学院地质研究所博士生李云帅协助完成相关数据处理工作; 审稿专家及责任编辑杨艳老师对论文提出了宝贵修改意见, 在此一并表示感谢!

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