

Salty Matters

John Warren - Friday Nov 13, 2015

Lapis Lazuli: one of the many metamorphosed evaporite precious stones and gems

Introduction

Precious stones and gems are rare by definition; hence need exceptional geologic conditions to give rise to gem-quality materials. A nexus across most natural gem-forming environments is the requirement for hydrous typically saline to hypersaline solutions, apt to precipitate euhedral crystals in a void or a pressure shadow, from fluids that contain elevated and unusual levels of particular constituents, including chromophores; hence pegmatites, volcanics and meta-evaporites are commonplace hosts for natural gemstones. Fluids promoting the growth of gem-quality crystals typically include the availability of uncommon major constituents, along with the presence of adequate chromophores, as well limited concentrations of undesirable elements. Another need is open fluid space in an environment conducive to growing crystals of sufficient size and transparency. This general statement of requirements to form a precious stone also encapsulates why some gems have meta-evaporitic associations.

We know that depositional units of evaporite salts typically disappear or transform into other mineral phases by the early greenschist phase (Warren, 2016). As this happens the dissolution/transformation releases a pulse of hot basinal chloride waters that can carry gold and base metals (topics for another blog) as well as leaching and carrying elements such as beryllium, chromium and vanadium (chromophores) from adjacent organic-rich shales. Trace elements also tend to be enriched in the more evolved depositional brines that precipitate in later minerals in a primary evaporite precipitative series. Later, at the same time as halite dissolves or transforms on entry into the metamorphic realm, anhydrite layers and masses typically remain into the more evolved portions of the metamorphic realm (amphibolite-granulite facies). The volume loss associated with the dis-

solution/transformation of meta-evaporites facilitates the formation of open fluid space (sometimes pressurized) in veins and fractures so favoring sites that then allow the free growth of precious stones and euhedral ruby, tourmaline and emerald gemstones.

I am not saying all precious stones and gems are associated with evaporites, many natural gemstone settings are not, but the lapis lazuli of Afghanistan, the melon-sized perfect rubies of Myanmar, the prolific emerald fields in Columbia, and the tsavorite deposits of east Africa likely are (Garnier et al., 2008; Giuliani et al 2005; Feneyrol et al., 2013). In this article I will focus on lapis lazuli, for a discussion of other semi-precious stones and gems that are meta-evaporites see Chapter 14 in Warren (2016).

Lapis lazuli

Lapis Lazuli is the metamorphic remnant of a sodic-rich, quartz-absent, evaporite mineral assemblage. It is composed of an accumulation of minerals not a single mineral (unlike rubies and emeralds); it is mostly lazurite $(\text{Na, Ca})_8(\text{AlSiO}_4)_6(\text{S, SO}_4, \text{Cl})_{1-2}$, typically at levels of 30-40%. Lapis gemstone also contains calcite (white veins), sodalite (blue), and pyrite (gold flecks of color). Dependent on metamorphic history and protolith chemistry, other common minerals in lapis include; augite, diopside, enstatite, mica, haüyaneite, hornblende, and nosean.

Others	Nepheline	$8[(\text{Na,K})\text{AlSiO}_4]$	Si depleted lavas where Na rather than K
	Cancrinite	$4[(\text{Na}_6, \text{Ca})_2(\text{SiAlO}_4)_6(\text{CO}_3, \text{SO}_4, \text{Cl})_2 \cdot n\text{H}_2\text{O}]$	Effervesces with HCl; Si depleted lavas
	Leucite	$16[\text{KAlSi}_2\text{O}_6]$	Carbonatite component Si-depleted
Lapis lazuli components	Sodalite	$\text{Na}_8\text{Cl}_2(\text{AlSiO}_4)_6$	Royal blue colour, mineral of sodalite group; <i>Var.</i> hackmanite is tenebrescent
	Haüyne	$(\text{Na,Ca})_8(\text{Al,Si})_{12}\text{O}_{24}(\text{Cl,SO}_4)$	Variable colour, mineral of sodalite group, aka roeblingite
	Nosean	$\text{Na}_8(\text{SO}_4)(\text{AlSiO}_4)_6 \cdot \text{H}_2\text{O}$	Variable colour, solid solution series between nosean and hauyne, mineral of sodalite group, aka noselite
	Lazurite	$(\text{Na,Ca})_8(\text{Al,Si})_{12}(\text{O,S})_{24}(\text{SO}_4)(\text{Cl,OH})_2$	Ultramarine, mineral of sodalite group, bulk of the mineral constituents in Lapis lazuli. That name is from the Persian <i>lazward</i> for blue

Table 1. Feldspathoids and lapis lazuli.

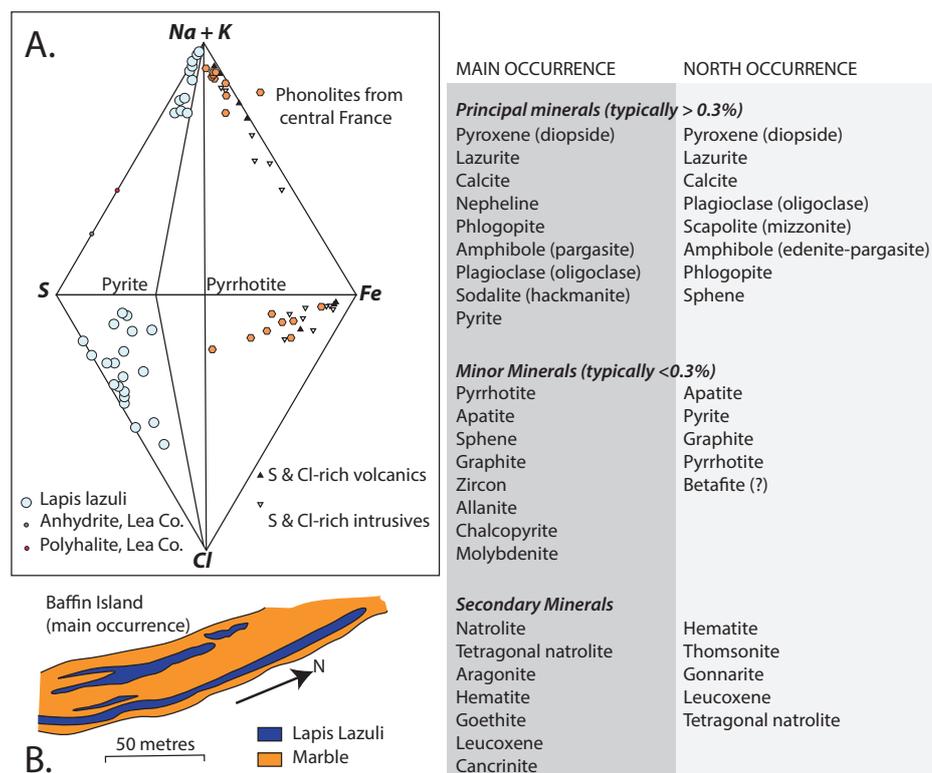


Figure 1. Lapis Lazuli and Baffin Island. A) Collateral compositional diagram, showing the relation between chlorine, iron, alkalis and sulphur for lapis lazuli from Baffin Island and Slyudyanka as well as alkalic igneous rocks and typical Permian evaporites for comparison. B) Baffin Island, map of the Main (South) occurrence shows the lapis lazuli distribution is stratiform within its dolomitic marble host. Also listed are major and minor mineral phases for the Main (South) and North occurrences (after Hogarth and Griffin, 1978)

ing sulphur and calcium content, while a green color is the result of insufficient sulphur (O'Donoghue, 2006, p. 329).

Other members of the sodalite group include sodalite and nosean (Table 1). Sodalite is the most sodium-rich member of the sodalite group and differs from the other minerals of the group in that its lattice retains chlorine. Interestingly, sodalite can be created in the laboratory by heating muscovite or kaolinite in the presence of NaCl at temperatures of 500°C or more. In the literature, the commonly accepted origin of lazurite is through contact metamorphism and metasomatism of dolomitic limestone. Such a metasedimentary system also requires a source of sodium, chlorine and sulphur; the obvious source is interbedded evaporites in the protolith, as is seen in plots of its molecular constituents (Aleksandrov and Senin, 2006).

Lapis lazuli from the Precambrian of Baffin Island, Canada (Figure 1), and from Edwards, New York, are meta-evaporites with evaporite remnants (anhydrites) remaining in the same series, as are the lapis lazuli deposits at Sar-e-Sang in the Kokcha valley, Afghanistan and the lapis deposits in Liadjuar-Dara region ("River of Lazurite") at an altitude of 5000 m in the Pamir Mountains, Tajikistan (Webster, 1975). Throughout history its bright blue color has made lapis, mostly from Sar-e-Sang, a valued gem commodity. First mined 6000 years ago, the Sar-e-Sang lapis was transported to Egypt and present day Iraq and later to Europe where it was used in jewelry and for ornamental stone. Europeans even ground down the rock into an expensive powdered pigment for paints called "ultramarine".

Lapis deposits in Lake Harbor on Baffin Island and in the Edwards Mine, New York, were produced by high-grade metamorphism of a sulphate-halite-marble protolith (Hogarth and Griffin, 1978). The anhydrites preserved near Balmat are remnants of this sequence. On Baffin Island the two main lapis lazuli lenses, some 1.6 km apart, lie at the structural top of two sequences of dolomitic marble, the thicker lens being approximately 150 m across (Figure 1b). The elongation of both lenses parallels the local layering and foliation and shows a well-developed layering parallel to the regional foliation, giving additional evidence of its sedimentary protolith to the deposits. The Main and Northern bodies constitute diopside-lazurite rocks of variable gem quality and are localized in marbles among biotite gneisses. The Main (Southern) occurrence is as long as 170 m and 6 m thick. In these deposits, sheets of high-quality lazurite (up to 1 m thick) contain variable amounts of relict diopside and plagioclase, as well as newly formed haüyne, nepheline, or phlogopite. The quantitative proportions of these minerals define the color of the rock, which changes to a more intense blue with heating. The Northern occurrence (25×36 m in size) is less rich than the Main occurrence and consists of small (no more than 1 m) lenses showing disseminated lazurite, which imparts a bluish green color to the polished surface of the rock. Chlorine and sulphur

Some specimens also contain trace amounts of the sulphur-rich mineral lollingite (var. geyerite). Lazurite is a member of the sodalite group of feldspathoid minerals (Table 1). Feldspathoids have chemistries that are close to those of the alkali feldspars, but are poor in silica. If free quartz were present at the time of formation it would have reacted with any feldspathoid precursor to form feldspar not lazurite. Natural lazurite contains both sulphide and sulphate sulphur, in addition to calcium and sodium, and so is sometimes classified as a sulphide-bearing haüyne (Figure 1). Sulphur gives lazurite its characteristically intense blue color, which comes from three polysulphide units made up of three sulphur atoms having a single negative charge. The S³⁻ ion in the sulphur has a total of 19 electrons in molecular orbitals and a transition among these orbitals produces a strong absorption band at 600 nm, giving a strong blue color, with yellow overtones. The intensity of the gem's blue is increased with increasing

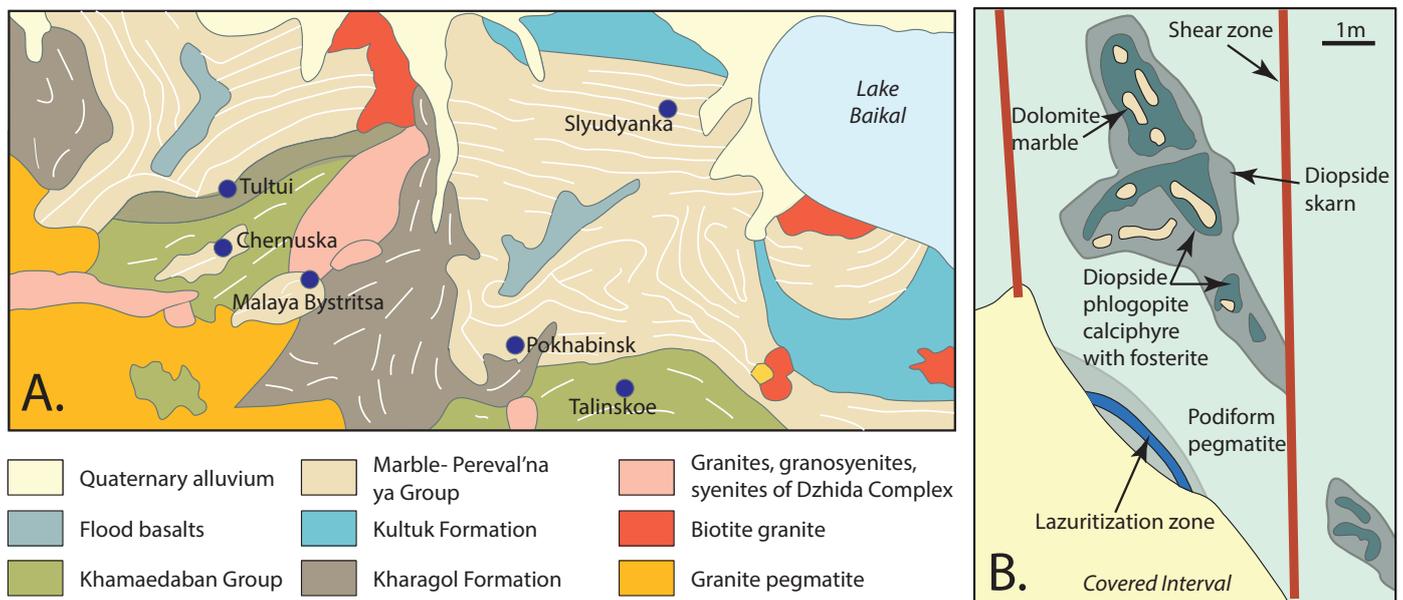


Figure 2. Lapis Lazuli geological setting. A) Geological map of the lazurite-bearing region in the southwestern Baikal area, also showing positions of main deposits and structural trend lines. B) Geological detail of a lapis occurrence at Sar-e-Sang Afghanistan (after Aleksandrov and Senin, 2006).

in the various lazurites, accessory pyrite, and pyrrotite were derived from metamorphosed gypsum-, anhydrite-, and evaporitic-carbonate protoliths (Hogarth and Griffin, 1978).

In the Lake Baikal lazurite occurrences, there is once again a strong association between marble of the Peralva Group and lazurite occurrence (Figure 2a). For example, the Slyudyanka deposit is hosted in diopside skarns and spinel–forsterite calciphyres, developed from metamorphically-evolved evaporitic dolomites (Aleksandrov and Senin, 2006). The Slyudyanka deposit shows clearly pronounced metasomatic zoning, which was associated with the prograde magnesian skarn stage and was overprinted by retrograde postmagmatic assemblages, that formed together with lazurite-bearing rocks under the influence of saline alkaline S–Cl-bearing hydrothermal solutions. These solutions also caused microclinization of blocks of leucocratic granite with the formation of lazurite in the some of the inner skarn zones. Potassium solutions caused phlogopitization of the host rocks.

Likewise, scapolite and magnesian whiteschists are typically saline mineral phases in the classic deposits of the Sar-e-Sang District (Figure 2b; Faryad, 2002). There, the lapis is composed of a combination of lazurite, diopside, calcite and pyrite and occurs in beds and lenses up to 4 meters thick within a scapolitic magnesian-marble skarn near the center of the Hindu Kush granitic massif. It is typically interlayered with, or forms veins and lenses within a gneissic and pegmatitic host. Lens-shaped lodes are typically hosted in orthoclase–microcline–perthite hornfels containing albite and quartz (Figure 2b). Lazurite bodies at the Sar-e-Sang deposit are associated with diopside metasomatites bearing nepheline, pale blue haüyne, and blue lazurite, and some lazurite-rich zones can contain up to 40–90 vol% lazurite. The rocks also contain diopside, haüyne, afghanite, and nepheline, as well as disseminated pyrite replaced by pyrrotite. Pockets of near pure lapis lazuli can be up to 40m across and occasionally up to a meter.

Lapis lazuli in the North Italian Mountains of Colorado occurs in impure marbles in a meta-evaporitic skarn near the contact with the Eocene-age quartz monzonite and quartz diorites of the Italian Mountain stocks (Hogarth and Griffin, 1980; Mauger, 2007). There, near vertical Pennsylvanian black shales and carbonates along the west margin of the intrusive have been converted to phlogopite–diopside–andalusite hornfels and scapolite–diopside skarns with minor analcime. Compared to Sar-e-Sang, lapis in this skarn deposit is of inferior quality. It forms as deep blue lazurite granules in fine-grained forsterite–Ti phlogopite–calcite skarns and calcite marbles with diopside, Ti–phlogopite and pyrite. The hosting sediments (Mississippian limestones and Devonian sandstones) define along the NE margin of the pluton, while the NaCl came from dissolution of once nearby halite or dissolution-derived saline surface waters and shallow groundwaters moving south from the Eagle Basin.

High quality lapis is also mined from a limestone–granite skarn contact in the Chilean Andes (3500 m elevation) in the headwaters of the Cazadero and Vias River, Ovalle, Coquimbo, Chile. The lapis there is good quality, although somewhat paler than Sar-e-Sang and, like the Baikal lapis deposits of Russia, is associated with wollastonite not diopside, making it a less attractive gem. The Chilean lapis occurs in an association of phlogopite, sodalite, calcite and pyrite (Coenraads and Canut de Bon, 2000).

Meta-evaporites in the Sar-e-Sang region of Afghanistan exhibit mosaic equilibria across small volumes (in the cm³ range) within a talc–kyanite schist (whiteschist) host. The microscale mineral variations are characterized by variations in mineral assemblages con-

ventionally attributed to vastly different pressure/temperature conditions during regional metamorphism.

On the basis of petrographic and microprobe studies, these assemblages are attributed to three consecutive stages of metamorphism of a chemically exceptional rock with a composition that falls largely into the model system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Figure 3; Schreyer and Abraham, 1976). Stage 1, typified by Mg chlorite-quartz -talc and some paragonite, was followed during stage 2 by talc-kyanite, Mg gedrite-quartz and the growth of large dravites (magnesian tourmalines). Microprobe analyses of the phases, gedrite and talc, indicate variable degrees of sodium incorporation into these phases according to the substitution $\text{NaAl} \rightarrow \text{Si}$. In stage 3, pure Mg cordierite formed with or without corundum and/or talc, and the kyanite was partly converted into sillimanite. Pressure and temperature during this final stage of metamorphism was near 5-6 kb and 640°C .

Schreyer and Abraham (1976) concluded that chemical variations in the metamorphic fluids were generated by progressive metamorphism and mobilization of an evaporite deposit. Relict anhydrite and gypsum (rehydrated anhydrite) still occur in the Sar-e-Sang area. Whiteschists and the associated lapis lazuli deposits of the region are part of a highly metamorphosed evaporitic succession. Salts have largely vanished due to ongoing melting and volatilizations. The preservation of the three stage succession of mineral assemblages, across such small scales and yet related to each other through isochemical reactions, means that the main factors governing the metamorphic history of this whiteschist were compositional changes of the coexisting fluids with time. Under this scenario any pressure-temperature variations were subordinate and the chemistry of the fluids evolved as the evaporites underwent metasomatic alteration.

The sedimentary pelitic layers of this precursor evaporitic sequence first underwent a period of metamorphism in which fluid pressures approached lithostatic (stage 1). Subsequently at higher metamorphic grades, with the beginning of mobilization of the salts, the metamorphic fluids became increasingly enriched in ions such as Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , BO_3^{3-} , etc., so that water fugacity dropped considerably. This period is represented by stage 2 of the whiteschist metamorphism and was characterized by strong metasomatism that led, for example, to the growth of dravite and the amphibolite, gedrite. The physical and chemical character of stage 3 is less clearly defined. Kyanite/sillimanite inversion requires an increase in temperature or a decrease in pressure, or both; but changes in the composition of a coexisting gas phase may have played an additional role in the formation of cordierite.

Unlike classic metamorphic associations, the meta-evaporite-derived assemblage in Afghanistan may in a single thin section entrain mineral as-

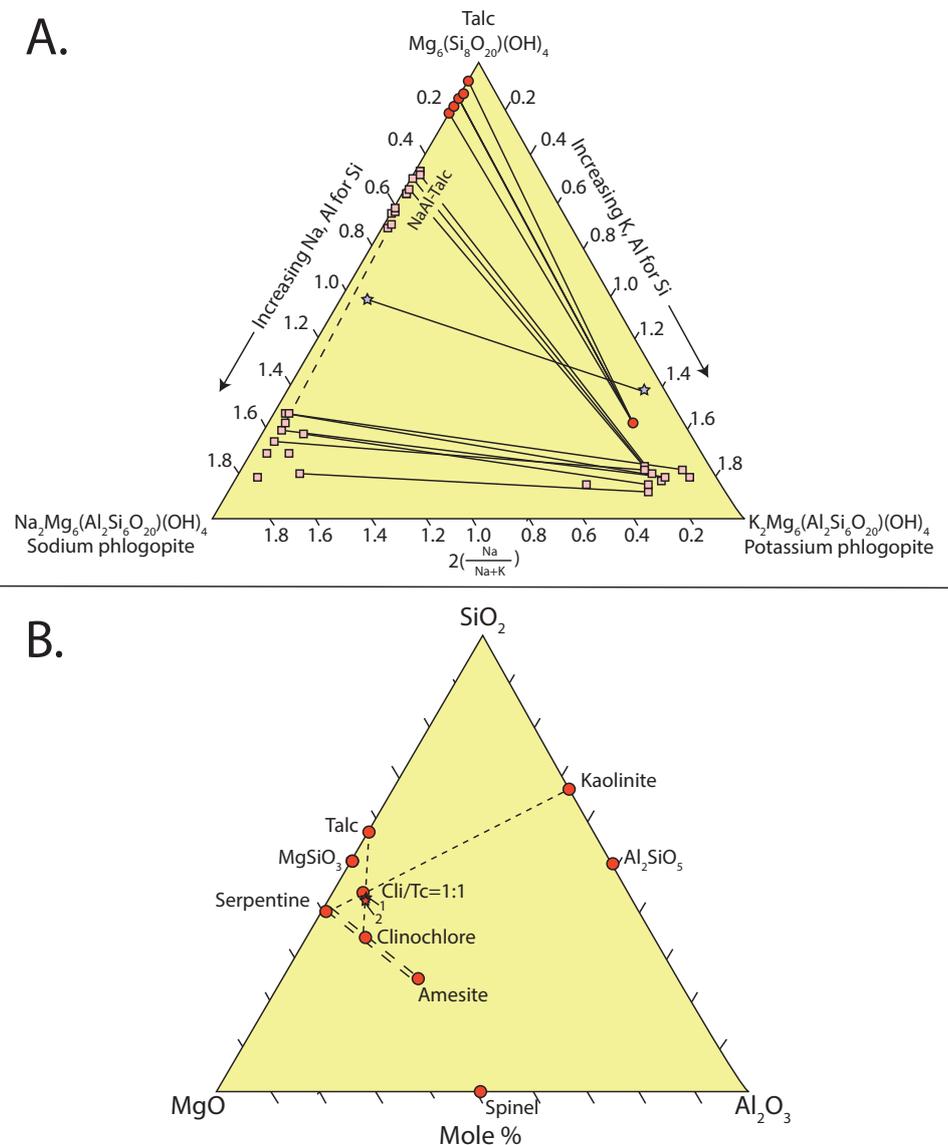


Figure 3. Sodion phlogopite, talc and kulkeite. A) Ternary system sodium phlogopite - potassium phlogopite - talc. Squares represent the 10 analyses from phlogopitic micas and the sodian aluminian talc. Circles indicate minerals from the Sar-e-Sang, Afghanistan, whiteschist (Schreyer and Abraham 1976), stars plot one set of coexisting micas from Post Pond, Vermont, metavolcanics. Solid lines connect coexisting phases, while the dashed tie line between talc and a sodium phlogopite represents the assemblage spread before the growth of potassium phlogopite (after Schreyer et al., 1980). B) Ternary plot of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ projected onto the water-free base showing some relevant crystalline phases, the location of a theoretical 1:1 clinocllore/talc mixture, and the analysed compositions of kulkeite indicated by stars 1 and 2 (after Schreyer et al., 1982).

semblages that conventionally would be assigned to the greenschist facies, the hornfels facies, and to a high pressure (amphibolite) regime. The assemblages are in effect mosaic equilibria that reflect changes in fluid composition generated from a metamorphosing evaporite pile over time and only to a lesser degree by regional evolution of total temperature and pressure. Once again, evaporites generate unusual responses compared to the general responses of metasediments.

In a refinement paper discussing the likely relationships between evaporites and whiteschists, Franz et al., 2013 note that whiteschist mineral assemblages are stable up to pressures of more than 4 GPa, but may already form at pressures of 0.5 GPa. Their formation largely depends on the composition of the protolith and requires elevated contents of Al and Mg as well as low Fe, Ca, and Na contents, as otherwise chloritoid, amphibole, feldspar, or omphacite are formed instead of kyanite or talc. They go on to note that the stability field of a whiteschist mineral assemblage strongly depends on XCO_2 and fO_2 : at low values of XCO_2 , CO_2 binds Mg to carbonates strongly reducing the whiteschist stability field, whereas high fO_2 enlarges the stability field and stabilizes yoderite $[Mg(Al,Fe^{3+})_3(SiO_4)_2O(OH)]$.

The scarcity of whiteschist is not necessarily due to unusual P-T conditions, but to the restricted range of suitable protolith compositions and the spatial distribution of these protoliths: (1) continental sedimentary rocks and (2) hydrothermally and metasomatically altered felsic to mafic rocks. They argue continental sedimentary rocks that may produce whiteschist mineral assemblages typically have been deposited under arid climatic conditions in closed evaporite basins and may be restricted to relatively low latitudes. These rocks typically contain large amounts of palygorskite and sepiolite. Franz et al., (2013) conclude whiteschist assemblages typically are only found in settings of continental collision or where continental lacustrine fragments were involved in subduction.

In my opinion, the mosaic signature of the precursor mineral phases in the typical Sar-e-San lapis lazuli is a metamorphically-evolved response to the combination of precursor permeability and stability contrasts typical of variably-cemented halite mosaic sediments in what were likely haloturbated and variably cemented saline continental lacustrine precursors.

References

- Aleksandrov, S., and V. Senin, 2006, Genesis and composition of lazurite in magnesian skarns: *Geochemistry International*, v. 44, p. 976-988.
- Coenraads, R., and C. C. de Bon, 2000, Lapis Lazuli from the Coquimbo Region, Chile: *Gems & Gemology*, v. 36, p. 28-41.
- Faryad, S. W., 2002, Metamorphic Conditions and Fluid Compositions of Scapolite-Bearing Rocks from the Lapis Lazuli Deposit at Sare Sang, Afghanistan: *Journal of Petrology*, v. 43, p. 725-747.
- Feneysel, J., G. Giuliani, D. Ohnenstetter, A. E. Fallick, J. E. Martelat, P. Monié, J. Dubessy, C. Rollion-Bard, E. Le Goff, E. Malisa, A. F. M. Rakotondrazafy, V. Pardieu, T. Kahn, D. Ichang'i, E. Venance, N. R. Voarintsoa, M. M. Ranatsenho, C. Simonet, E. Omito, C. Nyamai, and M. Saul, 2013, New aspects and perspectives on tsavorite deposits: *Ore Geology Reviews*, v. 53, p. 1-25.
- Franz, L., R. L. Romer, and C. Capitani, 2013, Protoliths and phase petrology of whiteschists: *Contributions to Mineralogy and Petrology*, v. 166, p. 255-274.
- Garnier, V., G. Giuliani, D. Ohnenstetter, A. E. Fallick, J. Dubessy, D. Banks, H. Q. Vinh, T. Lhomme, H. Maluski, A. Pecher, K. A. Bakhsh, P. Van Long, P. T. Trinh, and D. Schwarz, 2008, Marble-hosted ruby deposits from Central and Southeast Asia: Towards a new genetic model: *Ore Geology Reviews*, v. 34, p. 169-191.
- Giuliani, G., A. E. Fallick, V. Garnier, C. France-Lanord, D. Ohnenstetter, and D. Schwarz, 2005, Oxygen isotope composition as a tracer for the origins of rubies and sapphires: *Geology*, v. 33, p. 249-252.
- Hogarth, D. D., and W. L. Griffin, 1978, Lapis lazuli from Baffin Island; a Precambrian meta-evaporite: *Lithos*, v. 11, p. 37-60.
- Mauger, R. L., 2007, Contact metamorphism-metasomatism associated with the latest Eocene northern Italian Mountain granite intrusion, Gunnison County, Colorado: *Abstracts with Programs - Geological Society of America*, v. 39, p. 394.
- O'Donoghue, M., 2006, *Gems; Their Sources, Descriptions and Identification* (6th Edition): Amsterdam, Elsevier, 873 p.
- Schreyer, W., and K. Abraham, 1976, Three-stage metamorphic history of a whiteschist from Sar e Sang, Afghanistan, as part of a former evaporite deposit: *Contributions to Mineralogy & Petrology*, v. 59, p. 111-130.
- Von Rosen, L., 1990, Lapis lazuli in archaeological contexts, in P. Aströms, ed., *Studies in Mediterranean Archaeology and Literature*, v. 93, Partille, Sweden.

Warren, J. K., 2016, *Evaporites: A compendium* (ISBN 978-3-319-13511-3) Released Dec. 2015: Berlin, Springer, 1600 p.

Webster, R., 1975, *Gems, their sources, descriptions and identification*: London, Newnes, Butterworths.

Wood, J., 1841, John Wood. *A Personal Narrative of a Journey to the Source of the River Oxus by the Route of the Indus, Kabul, and Badakhshan, Performed under the Sanction of the Supreme Government of India, in the Years 1836, 1837, and 1838*. Available as Elibron Classics, 2001, 458 pages. Replica of 1841 edition by John Murray, London.



John Warren, Chief Technical Director
SaltWork Consultants Pte Ltd (ACN 068 889 127)
Kingston Park, Adelaide, South Australia 5049

www.saltworkconsultants.com

